SKINNER

Molecular Rearrangements
in the Camphor Series.
The Decomposition Products of the
Methyl Ester of Isoaminocamphonanic Acid

Chemistry

A. M.

1915

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. THE DECOMPOSITION PRODUCTS OF THE METHYL ESTER OF ISOAMINOCAMPHONANIC ACID

BY

GLENN SEYMOUR SKINNER
A.B. Kansas Manual Training Normal, 1913

THESIS

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UNIVERSITY OF ILLINOIS

1915

UNIVERSITY OF ILLINOIS
THE GRADUATE SCHOOL

June 5 1915

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY GLENN SEYMOUR SKINNER

ENTITLED MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. THE DECOMPOSITION PRODUCTS OF THE METHYL ESTER OF ISOAMINOCAMPHONANIC ACID.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ARTS

W. A. Noyes
In Charge of Thesis

W. A. Noyes
Head of Department

Recommendation concurred in:*

Committee on Final Examination*

*Required for doctor's degree but not for master's.

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I HISTORICAL

The Camphors.

The camphors may be regarded as simple oxidation products of a series of hydrocarbons having the empirical formula $(C_5H_8)_x$. These hydrocarbons, which together with their oxidation products, form a large number of the essential and naturally occurring oils, may be divided into four main classes:

Hemiterpenes	C_5H_8
Normal Terpenes	$C_{10}H_{16}$
Sesquiterpenes	$C_{15}H_{24}$
Polyterpenes	$(C_5H_8)_x$

Among the most important camphors derived from the normal terpene division are to be found Japan Camphor and Matricia Camphor. They are bicyclic ketones having the general formula $C_{10}H_{16}O$, but differing in the fact that one rotates the plane of polarized light to the right and the other an exactly equivalent degree to the left. The common or dextro variety occurs chiefly in the camphor laurel, Cinnamonum Camphora, a tree native to Japan, Formosa and central China. Laevo, or Matricia camphor is found in the volatile oil of the feverfew, Pyrethrum Parthenium[1], a European shrub, and in the twigs of the North American sage brush, Artemesia nana[2]. A mixture of equal parts[3] of the two gives racemic camphor, which is inactive. Synthetic camphor is also inactive. Victor Meyer[4] first proposed a formula for d-camphor in 1870. Since that time more than thirty

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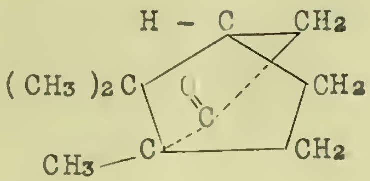
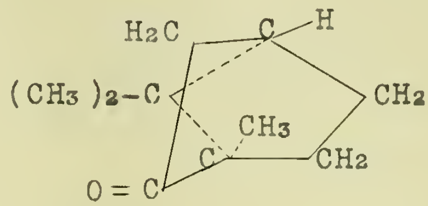
1. Compt.rend., 37, 66
2. Centr., (1900) 11, 2160
3. Ber., 12, 1756; 41, 4473
4. Ber., 3, 121.

formulas have been brought forward by nearly as many investigators, but the one now almost universally accepted is the one proposed by Bredt[1] in 1893. The relation between the two may be represented as follows:



d-Camphor
M. P. = 178.4°
α D = +42.22°



l-Camphor
M.P. = 178.4°
α D = −42.22°

THE CAMPHORIC ACIDS.

By oxidation with nitric acid each of the above camphors gives a dicarboxyllic acid[2,4]. Upon heating either acid in sealed tubes a partial conversion to an isomeric form[3,5] occurs, in which the secondary carboxyl shifts from the cis to the trans position. A mixture of equal parts of the two original acids gives racemic camphoric acid and a similar mixture of the isomeric acids gives racemic isocamphoric acid. Thirteen camphoric acids are described in the literature, but in 1894 Aschan[6] showed that there are only six.

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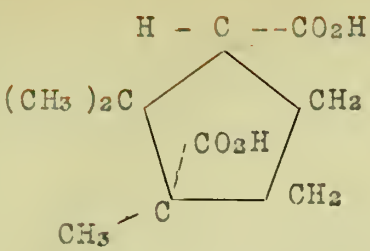
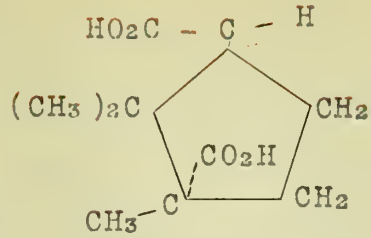
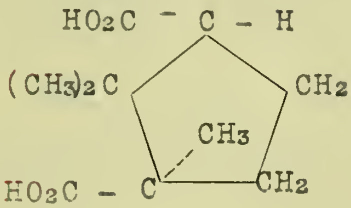
1. Ber., 26, 3049.
2. Ber., 36, 4332.
3. Compt. rend., 108, 979; J. Ch. Soc., 77, 386; Ber., 26, 1639; 28, 2151; Ann. 309, 341; Ber., 27, 2005; J. Am. Ch. Soc., 32, 1669; 35, 77; 36, 118.
4. Ann., 316, 210; 127, 121; Compt. rend., 56, 698; 110, 792; Jsb. Chem., 1853, 430; 1863, 556; Ber., 41, 4470; 42, 485.
5. Ann., 316, 211; Compt. rend., 110, 792; Ber., 27, 2005.
6. Ann., 127, 121; Compt. rend., 56, 698; Ber., 12, 1756; 105, 66,29, 1700; Compt. rend. 108, 979; Ber., 27, 2001.



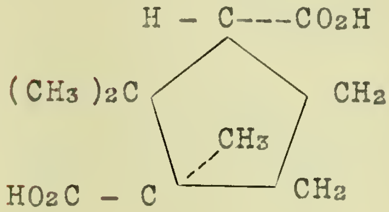
d-Camphoric Acid
M.P. = 187°
α_D = +49.7°



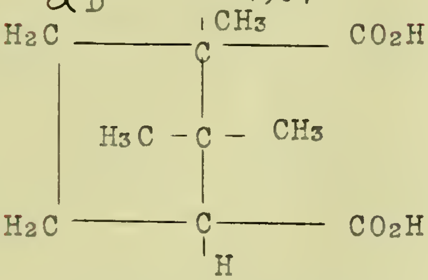
l-Isocamphoric Acid
M.P. = 172°
α_D = -47.6°



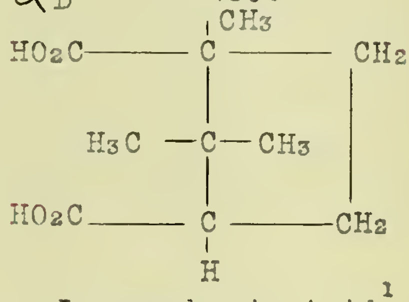
l-Camphoric Acid
M.P. = 187°
α_D = -49.7°



d-Isocamphoric Acid
M.P. = 171°-172°
α_D = +48.6°



r-Camphoric Acid[1]
M.P. = 202°-203°
α_D = (Inactive)



r-Isocamphoric Acid[1]
M.P. = 191°
α_D = (Inactive)

THE METHYL ESTERS OF d-CAMPHORIC AND OF l-ISOCAMPHORIC ACID.

It will be noticed from the formulae given for the camphoric acids that one of the carboxyls is linked to a secondary, while the other is linked to a tertiary carbon atom. Substituents in the former position are designated by the prefix ortho or α and these in the latter position by allo or β. In the present paper α and

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1. Ann., 127, 121; Compt. rend., 56, 698; Ber., 12, 1756; 105, 66, 29, 1700; Compt. rend., 108, 979; Ber., 27, 2001.

β will be used. The six methyl esters of d-camphoric and l-iso-camphoric acid theoretically possible have been prepared.

	B.P.	M.P.	
α,β-Methyl d-Camphorate[1]	155° (15 mm.)	(Liquid)	+48.16°
α-Methyl d-Camphorate[2]	223° (21 mm.)	77° -78°	+51.52°
β-Methyl d-Camphorate[3]		85° -86°	+43.55°
α,β-Methyl l-Isocamphorate[4]	146° (27 mm.)	(liquid)	-63.6°
α-Methyl l-Isocamphorate[5]		88°	-57.9°
β-Methyl l-Isocamphorate[6]		(liquid)	-53.1°

The speed of esterification for the secondary carboxyl is much greater than that for the tertiary. Thus the α methyl esters may be prepared in good yield by boiling with methyl alcohol and sulphuric acid for about twenty minutes, while a good yield of the α,β methyl esters is obtained only after boiling for several hours. Just as the α carboxyl is the more easily esterfied so it is the more easily saponified. Consequently by boiling with alkali for the proper length of time almost quantitative yields of the β methyl esters are obtained.

THE METHYL ESTERS OF d-CAMPHORAMIDIC AND l-ISOCAMPHORAMIDIC ACIDS.

Each of the acid esters of d-camphoric and l-isocamphoric acid gives an amide ester by the action of ammonia on the acid chloride obtained by treating the ester with phosphorus pentachloride. Their

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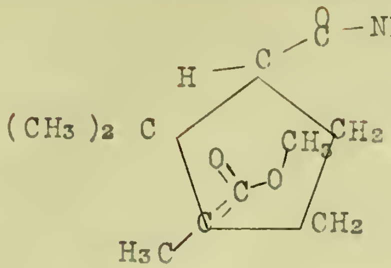
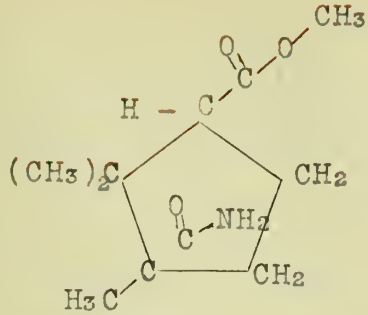
1. Ber., 25, 1809; 25(2), 665; Compt. rend., 114, 1517; J. Ch. Soc. 61, 1092; Monatsheft, 20, 687; Centr., 1908 (1), 424.
2. Ann. (3) 38, 483; Ber., 25, 1807; 26, 285; Compt. rend., 114, 1516; 116, 148; J. Ch. Soc., 61, 1090; 77, 377; Monatsheft, 20, 686.
3. Compt. rend., 114, 1518; 141, 698; Ber., 25 (2), 665.
4. J. Am. Ch. Soc., 32, 1671; 35, 77.
5. J. Am. Ch. Soc., 32, 1671; 35, 77.
6. J. Am. Ch. Soc., 35, 77.

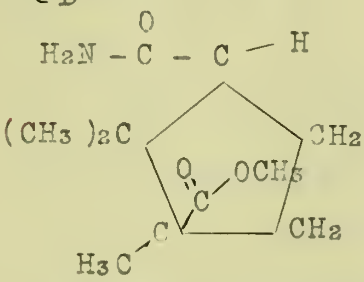
structural formulas follow:



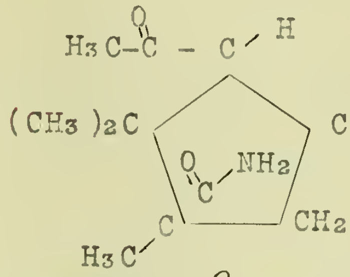
β-Methyl α-d-Camphoramidate
M.P. = 148°
α_D = +23.33



α-Methyl β-d-Camphoramidate
M.P. = 139
D = +57.25



β-Methyl α l-Isocamphoramidate
M.P. = 126 - 127
α_D = -54.1



α-Methyl β l-Isocamphoramidate
M.P. = 157
α_D = -60.08

β-METHYL α d-CAMPHORAMIDATE was first obtained by Van der Meulen[1] (1896), who obtained it by treating a methyl alcohol solution of cyanocamphonanic[3] acid, $C_8H_{14}\begin{matrix}-CN\\ -CO_2H\end{matrix}$, or of α-camphoric-isoimide, $C_8H_{14}\begin{matrix}-C=N-H\\ \;\;\;\;>O\\ -C=O\end{matrix}$, with gaseous hydrogen chloride. Haller[2] (1895) also obtained it by the action of ammonia on β-methyl camphorate.

α-METHYL β-d-CAMPHORAMIDATE was prepared by Noyes[4] (1894) by the action of ammonia on α-methyl β camphoryl chloride. Van der Meulen[1] (1896) obtained it by the action of gaseous hydrogen chloride on a methyl alcohol solution of the free acid, or of β-camphor isoimide, $C_8H_{14}\begin{matrix}-C=O\\ \;\;\;\;>O\\ -C=N-H\end{matrix}$. Haller[2] (1905) obtained it

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1. Recueil, 15, 323.
2. Compt. rend., 141, 697.
3. J. Am. Ch. Soc., 34, 1067 (1912).
4. Ber., 27, 918; Am. Ch. J., 16, 308.

by treating α-methyl β camphoryl chloride with ammonia.

β-METHYL α l-ISOCAMPHORAMIDATE was prepared by Noyes and Littleton[1] (1913) by the action of ammonia on β-methyl α-l-isocamphoryl chloride.

α-METHYL β l-ISOCAMPHORAMIDATE was prepared by Noyes and Knight[2] (1910) by treating α-methyl β l-isocamphorylchloride with ammonia.

THE d-CAMPHORAMIDIC AND l-ISOCAMPHORAMIDIC ACIDS.

d-CAMPHORAMIDIC acid was prepared as the ammonium salt by Malaguti[3] (1837) by the action of gaseous ammonia on an alcoholic solution of d-camphoric anhydride. This substance was later identified by Laurent[4] (1846). It was prepared in the same manner by Ballo[5] (1879). Auwers and Schnell[6] (1893) obtained it by the action of aqueous instead of gaseous ammonia upon d-camphoric anhydride. It was obtained by Noyes[7] (1894), and by Hoogewerf and Van Dorp[8] (1895) in a similar manner. It has also been obtained by warming isonitroso camphor,[9] $C_8H_{14}\left\{\begin{array}{l}-C=N-OH\\ -C=O\end{array}\right.$, with fuming hydrochloric acid and by the decomposition of the chloroplatinate[10] of the hydrochloride of α-camphornitrilic acid with water.

M. P.[3] = 176 - 177 $\qquad \alpha_D$ = +45

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1. J. Am. Ch. Soc., 35, 79.
2. J. Am. Ch. Soc., 32, 1671.
3. Ann., 22, 42.
4. Ann., 60, 327.
5. Ann., 197, 321.
6. Ber., 26, 1522.
7. Am. Ch. J., 16, 502; Ber., 27, 918.
8. Receuil, 14, 251.
9. Ann., 274, 71; Ber., 26, 242.
10. Gazz. chim. ital., 26 (1), 416.

β-d-camphoramidic acid was first prepared by Noyes[1] (1894) by heating d-camphoric imide, $C_8H_{14}\left\langle\begin{matrix}-C=O\\ NH\\ -C=O\end{matrix}\right.$, with 10 per cent sodium hydroxide solution. Hoogewerf and Van Dorp[2] (1895) prepared it by the same method and showed that it is formed in small amount with the α-d-camphoramidic acid when an alcoholic solution of camphoric anhydride is treated with ammonia.

M.P.[2] = $180^{\circ} - 181^{\circ}$. α_D[2] = $+60^{\circ}$.

β, l-ISOCAMPHORAMIDIC ACID was prepared by Noyes and Knight[3] (1910) by the saponification of α-methyl β-l-isocamphoramidate.

M.P. = $165^{\circ} - 166^{\circ}$. α_D =

α, l-ISOCAMPHORAMIDIC ACID has not been prepared.

THE AMINO ACIDS WHICH ARE DERIVED FROM THE d-CAMPHORAMIDIC AND l-ISOCAMPHORAMIDIC ACIDS

These acids have been prepared from the corresponding acid amides by Hofmann's reaction.

AMINOCAMPNONANIC ACID[4] (AMINOLAURONIC) is derived from β-d camphoramidic acid. It forms an anhydride which yields a nitroso derivative with nitrous acid. M. P. 260°. $\alpha_D = -29.1^{\circ}$. Hydrochloride, M. P. = $303^{\circ} - 305^{\circ}$. $\alpha_D = +24.9^{\circ}$.

DIHYDROAMINOCAMPHOLYTIC ACID[5] is derived from β-camphoramidic acid. It forms an anhydride which yields a nitroso derivative with nitrous acid. M. P. = (Sublimes). $\alpha_D = +54.5$. Hydrochloride, M. P. = $261^{\circ} - 262^{\circ}$. $\alpha_D = +44.5^{\circ}$.

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1. Am. Ch. J., 16, 502; Ber., 27, 918.
2. Receuil, 14, 251.
3. J. Am. Ch. Soc., 32, 1671.
4. Am. Ch. J., 16, 503; 17, 432; 18, 3; Ber., 33, 2963; J. Ch. Soc., 99, 1270.
5. Am. Ch. J., 16, 503; 16, 310; 17, 421; 24, 290.

ISOMINOCAMPHONANIC (ISOAMINOLAURONIC) ACID[1] is derived from l-isocamphoramidic acid. No anhydride has been prepared. Hydrochloride, M. P. = 320° (cor.).

ISODIHYDROAMINOCAMPHOLYTIC ACID[2] is derived from β,l-isocamphoramidic acid. By boiling with acetic anhydride it yields the anhydride of dihydroaminocampholytic acid. M. P. = 235° - 236° (decomp.). α_D = -32.9°. Hydrochloride, M. P. = 296° - 298°. α_D = -45.0°.

THE METHYL ESTERS OF THE AMINOACIDS WHICH ARE DERIVED FROM THE METHYL ESTERS OR THE d-CAMPHORAMIDIC AND l-ISOCAMPHORAMIDIC ACIDS.

METHYL AMINOCAMPHONANATE has not been prepared.

METHYL DIHYDROAMINOCAMPHOLYTATE has been prepared by Noyes[3] (1894). It is an oily liquid. The hydrochloride melts at 244°.

METHYL ISOAMINOCAMPHONANATE has been prepared by Noyes and Littleton[4] (1912). It boils at 239° (cor.). The hydrochloride melts at 177°, and has a rotation of, α_D = -42.03 (in alcohol); -32.03 (in water).

METHYL ISODIHYDROAMINOCAMPHOLYTATE has not been prepared.

THE DECOMPOSITION PRODUCTS OF AMINOCAMPHONANIC ACID.[5]

Noyes and Taveau[6] by decomposing this acid with nitrous acid or the nitroso derivative of the anhydride with alkali obtained the following products:

1. J. Am. Ch. Soc., 35, 79.
2. J. Am. Ch. Soc., 32, 1671.
3. Am. Ch. J., 16, 308.
4. J. Am. Ch. Soc., 35, 80.
5. Am. Ch. J., 16, 508; 17, 432; 32, 288; 35, 379.
6. Am. Ch. J., 32, 288; 35, 379.

I. VOLATILE WITH STEAM.

1. A HYDROCARBON C_8H_{14} ----------B.P. = 122°.

2. ISOCAMPHOLACTONE $C_8H_{14}\left<\begin{matrix} C = O \\ | \\ O \end{matrix}\right.$ --M.P. = 32°; $\alpha_D = -60.7$

3. AN UNSATURATED ACID-----------B.P. = 130° - 133/21 mm.;
M.P. = 152° - 154°.

4. -LAURONOLIC ACID[1] $C_8H_{13}CO_2H$.

II. NOT VOLATILE WITH STEAM.

1. HYDROXYLAURONIC ACID $C_8H_{14}\left<\begin{matrix} OH \\ CO_2H \end{matrix}\right.$ B.P. = 180° - 185°/21 mm.

2. A NEW LACTONE $C_8H_{14}\left<\begin{matrix} O \\ \backslash \\ C = O \end{matrix}\right.$ ----B.P. = 126°/27 mm.;
M.P. = 164° - 165°.

THE HYDROCARBON has been identified by Noyes and Derick[2] as laurolene. The laurolene formed by the decomposition of the amino acid with nitrous acid is dextro rotatory, $\alpha_D^{25} = +22.8$, and that obtained by the decomposition of the nitroso derivative with alkali is laevorotatory, $\alpha_D = -14.5^\circ$. The correct formula for laurolene was proposed by Eijkman[3] and later confirmed by Noyes and Kyriakides[4].

ISOCAMPHOLACTONE[5] by hydrolysis gives a hydroxy acid, the silver salt and methyl ether[6] of which have been prepared. Its structure[7] is not yet known.

THE UNSATURATED ACID melting at 152° - 154° has not yet been investigated.

γ-LAURONOLIC ACID[8] gives campholactone on standing with di-

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1. J. Ch. Soc., 67, 341.
2. J. Am. Ch. Soc., 31, 670.
3. Chem. Weekblad, 1906, No. 15; 1907, No. 4; Chem. Centr., 1907 II, 1208.
4. J. Am. Ch. Soc., 32, 1064.
5. Am. Ch. J., 32, 290.
6. Am. Ch. J., 35, 381.
7. Ber., 35, 1292; J. Am. Ch. Soc., 31, 280.
8. J. Ch. Soc., 67, 341; J. Am. Ch. Soc., 34, 176; Am. Ch. J., 17, 434

lute sulphuric acid. It has never been obtained except as a viscous liquid and is probably a mixture of several isomeric acids. Campholactone has a specific rotation of $\alpha_D = -21.7^{\circ}$ and melts at 50°. The hydroxy acid from which it is derived has a specific rotation of $\alpha_D = +16.0^{\circ}$ and melts at 143°.

HYDROXYLAURONIC ACID[1] has been obtained only as a viscous liquid. It may be a mixture of several hydroxy acids.

THE NEW LACTONE has later[2] been shown to be identical with cis-camphonololactonewhich Bredt[3] prepared by the electrolytic reduction of camphononic acid. The pure lactone melts at $165^{\circ} - 167^{\circ}$ and has a specific rotation of $\alpha_D = -22.3$. The corresponding hydroxy acid is cis-camphonolic acid which has a specific rotation of $\alpha_D = +29.2$, and melts at $202^{\circ} - 203^{\circ}$, depending upon the rate of heating. Noyes and Taveau give the melting point of their hydroxy acid as 189.5°. The hydroxyl and carboxyl of cis-camphonolic acid are in the α and β positions respectively.

THE DECOMPOSITION PRODUCTS OF DIHYDROAMINOCAMPHOLYTIC ACID[4].

The decomposition products of dihydroaminocampholytic acid have been studied by Noyes and Potter[5] (1912). The compounds formed are the following:

ISOLAUROLENE--------------------------B.P. = $106^{\circ} - 110^{\circ}$.

l-CAMPHOLYTIC ACID--------------------- $\alpha_D = -70.0^{\circ}$

d-CAMPHOLYTOLACTONE--------------------M.P. = 118°-119°; $\alpha_D = +8.5^{\circ}$

d-TRANS-DIHYDROHYDROXYCAMPHOLYTIC ACID-M.P. = 133.7°; $\alpha_D = +70.1^{\circ}$

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1. J. Am. Ch. Soc., 31, 280.
2. J. Am. Ch. Soc., 34, 64.
3. Ann., 366, 1.
4. Am. Ch. J., 16, 311; 17, 424; 24, 290; Ber., 33, 2938.
5. J. Am. Ch. Soc., 34, 1067.

ISOLAUROLENE is optically inactive. Blanc[1] (1898) first proposed its correct structural formula, later (1906) establishing it by synthesis[2].

l-CAMPHOLYTIC ACID was first prepared by Walker[3] (1893) by the electrolysis of the sodium salt of α-ethyl d-camphorate, and saponification of the resulting ester. $\alpha_D = -50^\circ$. B. P. = $240^\circ - 242^\circ$. Noyes[4] (1894) prepared it by decomposing dihydroaminocampholytic acid. He showed[5] that upon standing with mineral acids it is changed to isocampholytic acid. Tiemann[6] prepared it in the same way. Noyes and Phillips[7] (1900) found the specific rotation to be $\alpha_D = -60.4$, and showed that distillation tends to racemize it. Noyes and Potter[8] found the rotation to be, -70.0°. Racemic campholytic acid has been prepared by the action of hydrogen bromide on isocampholytic acid[9], and by the reduction of β-campholytic acid[10]. Perkin and Thorpe[11] (1903) have synthesized the racemic acid. It boils at 127 - 128/14 mm., and melts at 31. Tiemann[12] (1900) and Blanc[13] (1901) have further demonstrated its structure by oxidation. Thus-,

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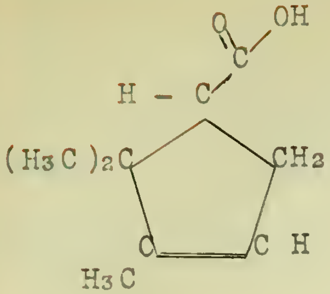
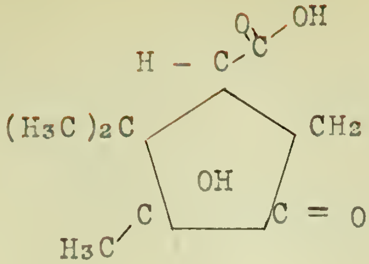
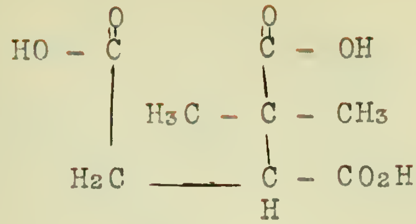
1. Bull., (3) 19, 699.
2. Compt. rend., 142, 1084.
3. J. Ch. Soc., 63, 498.
4. Am. Ch. J., 16, 505.
5. Am. Ch. J., 17, 428.
6. Ber., 33, 2938.
7. Am. Ch. J., 24, 290.
8. J. Am. Ch. Soc., 34, 1077.
9. J. Ch. Soc., 77, 380; Am. Ch. J., 26, 285; Bull. (3) 25, 81.
10. J. Ch. Soc., 83, 853.
11. J. Ch. Soc., 85, 147; Chem. Centr., 1903 (1), 923; 1904 (1), 727.
12. Ber., 33, 2939.
13. Bull., (3) 25, 81.



Campholytic Acid

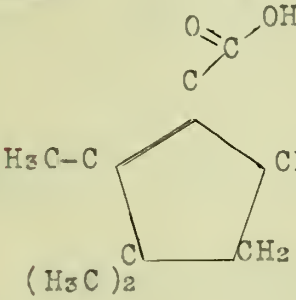


M. P. = 192°



Di-methyl Tricarballylic Acid
M. P. = 156° - 157°

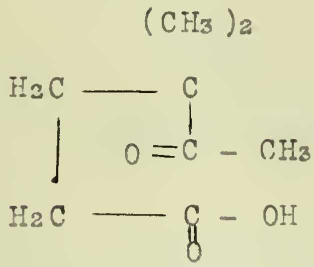
The structure of isocampholytic acid was shown in a similar manner by Blanc[1] (1899).



Isocampholytic Acid
(β-campholytic)
(Isolauronolic Acid)

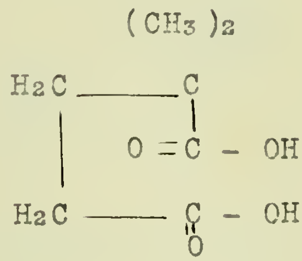
M. P. = 132°

α_D = (inactive)



3,3-Di-methyl, 4-keto, Hexanoic Acid

M. P. = 48°



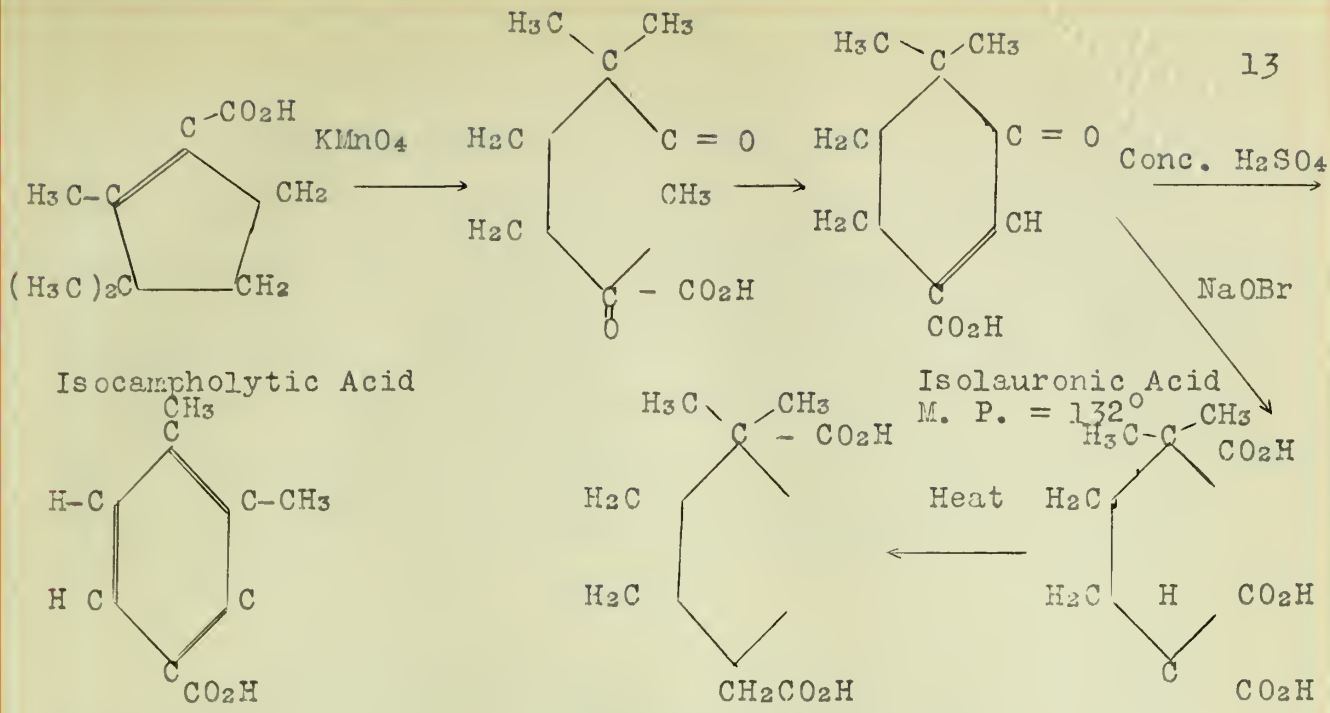
Di-methyl Glutaric Acid

M. P. = 84°-85°

Koenigs and Meyer (1894) had previously determined the structure of this acid by oxidation with potassium permanganate[2]. The isolauronic acid thus obtained gives by oxidation with sodium hypobromite α,α-dimethyl α-carboxy adipic acid, which under the influence of heat loses carbon dioxide, giving α,α-dimethyl adipic acid. By heating with concentrated sulphuric acid it is converted into paraxylic acid, which crystallizes in short needles[3]. These reactions may be represented as follows:

- -

1. Ann. (7) 18, 252.
2. Ber., 27, 3467.
3. J. Ch. Soc., 71, 167.



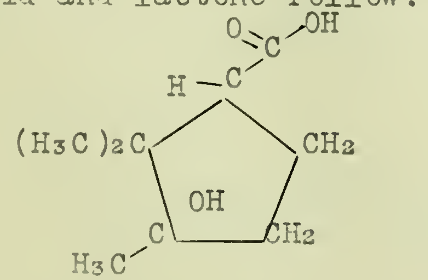
Isocampholytic Acid

Isolauronic Acid
M. P. = 132°

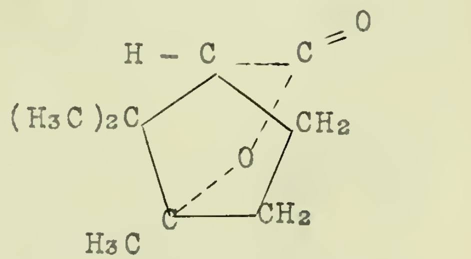
Paraxylic Acid
M. P. = 163°

α,α-Dimethyl Adipic Acid
M.P. = 87°

d-CAMPHOLYTOLACTONE was first obtained by Tiemann[1] (1900) by decomposing dihydroaminocampholytic acid with nitrous acid. Blanc[2] (1901) found that some campholytolactone was formed in the preparation of r-campholytic acid from isocampholytic acid with hydrogen bromide. Noyes and Potter[3] (1912) prepared it by decomposing the nitroso derivative of dihydroaminocampholytic acid. They regard the corresponding hydroxy acid as a cis compound. The formula of the acid and lactone follow:



d-cis-dihydrohydroxycampholytic Acid
(Campholytolic)
M. P. = 118.5°
α_D = +56.8°



d-Campholytolactone
M.P. = 118° -119°
α_D = +8.5°

1. Ber., 33, 2938.
2. Bull., (3) 25, 81.
3. J. Am. Ch. Soc., 34, 1075.

d-TRANS-DIHYDROHYDROXYCAMPHOLYTIC ACID was first prepared by Noyes[1] (1895) in the decomposition of dihydroaminocampholytic acid with nitrous acid. Tiemann[2] (1800) prepared it in the same manner. Noyes and Potter[3] (1912) obtained it by the decomposition of the nitroso derivative with sodium hydroxide and also by the decomposition of aminodihydrocampholytic acid with nitrous acid. The yields of the decomposition products were approximately as follows:

I. From the Nitroso Compound.

1. Isolaurolene---------------------------- 3.0 o/o
2. Campholytolactone---------------------- 4.0 o/o
3. Campholytic Acid----------------------- 7.0 o/o
4. Trans-Dihydrohydroxycampholytic Acid--45.0 o/o

II. From the Amino Acid.

1. Isolautolene---------------------------- 0.7 o/o
2. Campholytolactone---------------------- 5.3 o/o
3. Campholytic Acid----------------------- 2.0 o/o
4. Trans-hydroxydihydrocampholytic Acid--45.0 o/o

They have shown that it has a trans configuration, since it does not form a lactone when heated by itself or with water. By warming or allowing to stand over night with dilute sulphuric acid, isocampholytic acid is formed. Bredt[4] (1900) obtained the lactone however by continued heating with acetic anhydride. By heating with water in a sealed tube on the steam bath the following products are obtained:

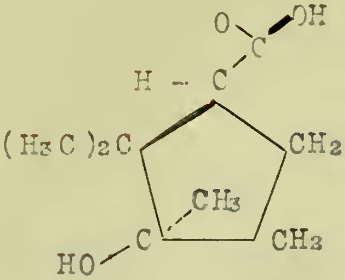
1. Isolaurolene---------------------------12.0 o/o
2. Campholytolactone--------------------- 7.0 o/o
3. Campholytic acid----------------------35.0 o/o
4. Trans-Dihydrohydroxycampholytic Acid--35.0 o/o

It is probably formed by a Walden inversion. The structure of

- -

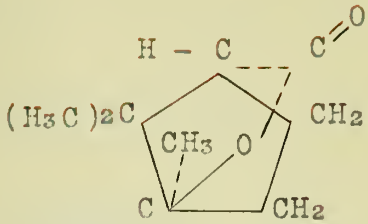
1. Am. Ch. J., 17, 424.
2. Ber., 33, 2938.
3. J. Am. Ch. Soc., 34, 1074.
4. Ann., 314, 392.

the acid and lactone are as follows:



d-Trans-Dihydrohydroxycampholytic Acid

M. P. = 133.7°
α_D = +70.1°



Lactone of d-Trans-Dihydrohydroxycampholytic Acid

M. P. = 115° - 117°
α_D = +121.9°

THE DECOMPOSITION OF ISOAMINOCAMPHONANIC ACID.

Noyes and Littleton[1] (1913) decomposed this acid with nitrous acid obtaining the following products:

1. CIS-CAMPHONOLOLACTONE------M.P.= 160°- 162°; α_D = -16.1°
2. AN UNSATURATED ACID--------B.P.= 150°/60 mm.
3. A DARK VISCOUS OIL---------------(Decomposes at 160°)

THE DECOMPOSITION OF ISODIHYDROAMINOCAMPHOLYTIC ACID.

Noyes and Knight decomposed[2] (1910) this acid with nitrous acid and obtained the following products:

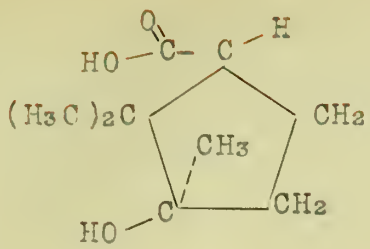
1. 1-DIHYDROHYDROXYCAMPHOLYTIC ACID -------------
2. AN UNSATURATED ACID, (Probably d-campholytic)α_D= +46.0°
3. A LACTONE-------------------------------------
4. A HYDROCARBON---------------------------------

Noyes and Nickell[3] continued the investigation and obtained the following:

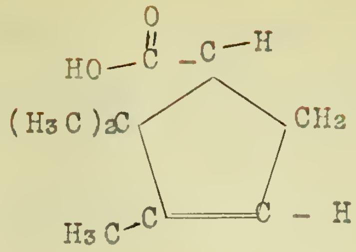
1. AN HYDROXY ACID------------M. P. = 132°
2. d-CAMPHOLYTIC ACID---------B. P. =
3. 1-CAMPHOLYTOLACTONE--------M. P. = 114°-115°; α_D= -8.2°
   B. P. = 228°-230°
4. A SMALL AMOUNT OF A HYDROCARBON (Probably isolaurolene)

- -

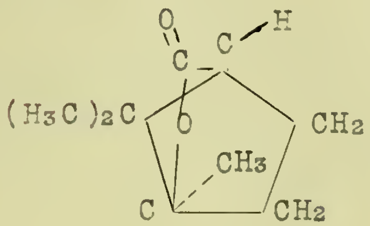
1. J. Am. Ch. Soc., 32, 1672.
2. J. Am. Ch. Soc., 32, 1669
3. J. Am. Ch. Soc., 36, 118.



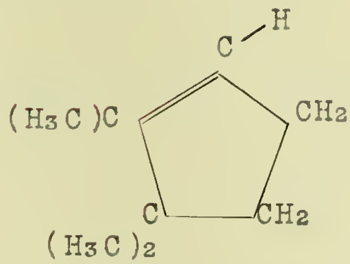
1-cis-Dihydrohydroxycampholytic Acid[1]
M. P. = 132°
α_D = -70.04°



d-Campholytic Acid[2]
B. P. =
α_D = +66.35°



1-Campholytolactone[2]
B. P. = 228° - 230°
M. P. = 114° - 115°
α_D = -8.2°



Isolaurolene
B. P. = 108° - 110°
α_D = (Inactive)

The structure of the lactone[2] was established by converting it into 1-cis-dihydrohydroxycampholytic acid, which has a specific rotation of $_D$ = -53.1° and melts at 117° - 118°.

It is thus clear that the compounds formed in the decomposition of the four amino acids in question fall into the following four classes:

1. UNSATURATED ACIDS $C_8H_{13}CO_2H$
2. HYDROXY ACIDS $C_8H_{14}(OH)CO_2H$
3. LACTONES $C_8H_{14} - C = O$ (with O bridging)
4. HYDROCARBONS C_8H_{14}

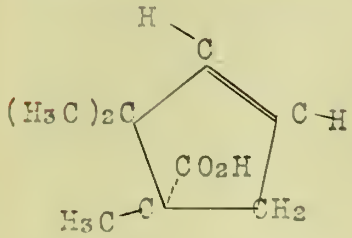
THE UNSATURATED ACIDS

Thirteen unsaturated acids of the general formula $C_8H_{13}CO_2H$,

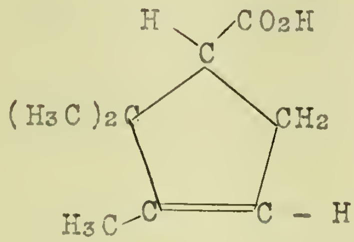
- -

1. J. Am. Ch. Soc., 32, 1669.
2. J. Am. Ch. Soc., 36, 118,

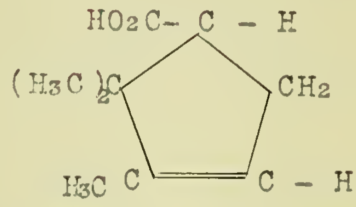
which are derived from the camphoric acids as shown in the preceding pages, have been prepared. Of this number the structure of eight are known.



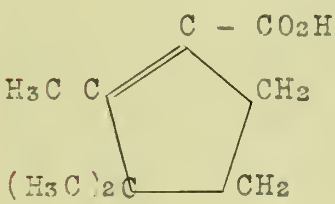
Dehydrolauronic Acid[1]
M. P. =
α_D =



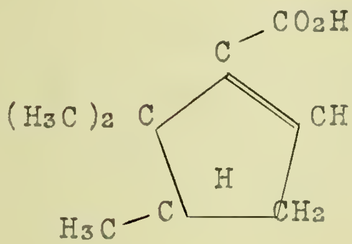
l- α Campholytic Acid[2]
B. P. = $240^\circ - 243^\circ$
α_D = -70°



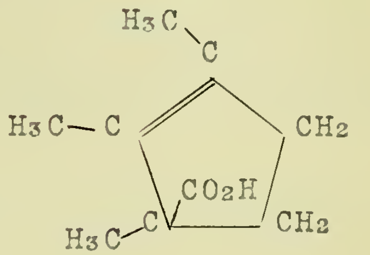
d- α Campholytic Acid[3]
B. P. =
α_D = $+66.35^\circ$



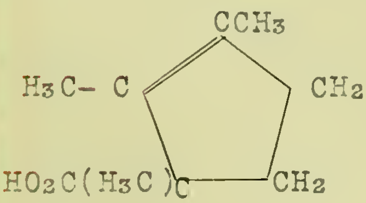
Isocampholytic Acid[4]
M. P. = 132°



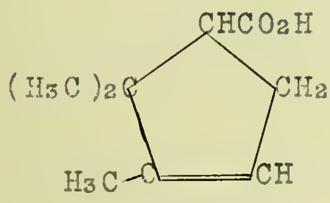
Δ^5-Acid[5]



Lauronolic Acid[6]
M.P. = $6.5^\circ - 8^\circ$
B.P. = $230^\circ - 235^\circ$
α_D = $+187.7^\circ$



i-Lauronolic Acid[7]
M. P. =. 5.8°



i-Campholytic Acid[8]
M. P. = 31°
B. P. = $127^\circ - 128^\circ$ (14 mm.)

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1. Ber., 35, 1286.
2. This Thesis, Page 11
3. This Thesis, Page 16
4. This Thesis, Page 12
5. Am. Ch. J., 26, 289; 22, 268
6. Ann., 227, 6; Ber., 27, 3504; 33, 3944; 33, 2944; J. Ch. Soc., 77, 1057; 79, 1289; Am. Ch. J., 16, 508; 17, 433; J. Ch. Soc., 67, 337.
7. J. Am. Ch. Soc., 34, 181.
8. Am. Ch. J., 26, 285; J. Ch. Soc., 77, 378.

Bredt[1] (1902) obtained dehydrolauronic acid by the dry distillation of the ester of dehydrocamphoric acid which he obtained by treating the diphenyl ester of chlorocamphoric acid with quinoline. He called this compound lauronolic acid but gave no physical constants for it. The structure given rests upon the fact that it gives camphoronic acid on oxidation.

The structures of l-α-campholytic acid and β-campholytic acid have been shown by methods previously described. The latter acid[2] is formed by treating α-campholytic, dihydrohydroxycampholytic, campholytolic, infracampholenic, or i-α-campholytic acid with dilute mineral acids. Koenig and Hoerlin obtained it from sulphocamphylic acid. By treating its hydrobromide with alkalies it is converted into α-campholytic acid.

The structure of d-α-campholytic acid is based upon its synthesis from isodihydrohydroxycampholytic acid and upon the fact that its optical rotation is practically equal and opposite to that of l-α-campholytic acid.

The structure[3] given the Δ^5 acid is the one most probable from its synthesis and also from the fact that it is not converted into isocampholytic acid by dilute mineral acids. Noyes and Blanchard (1901) obtained it by treating the α-bromine derivative of a dihydrocampholytic acid with alcoholic potash. The dihydrocampholytic acid was prepared by the reduction of the hydroiodide of r-α-campholytic acid.

Lauronolic acid gives by oxidation no trace of camphoronic acid. By heating with soda-lime it gives laurolene which has been

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1. Ber., 35, 1286.
2. Am. Ch. J., 17, 428; 27, 432; 26, 285; Ber., 33, 2937; 33, 2939; 26, 813; J. Ch. Soc., 79, 108: 77, 378.
3. Am. Ch. J., 26, 289; 22, 268.

shown to contain a 1,2,3 - trimethyl group. It has been prepared by treating aminocamphonanic acid with nitrous acid or the nitroso derivative of the anhydride with sodium hydroxide, by the dry distillation of camphanic acid either alone or in a slow current of carbon dioxide, by the electrolysis of the sodium salt of the β-ethyl ester of camphoric acid, and by the action of sodium carbonate on bromcamphoric anhydride.

i-Lauronolic acid is formed by the distillation of i-camphanic acid which is derived from synthetic camphor.

Inactive campholytic acid has been prepared by the decomposition of the hydrobromide of α-campholytic acid with sodium hydroxide. It has also been prepared from synthetic camphor[1] and is converted into β-campholytic acid by dilute mineral acids.

The γ-lauronolic acid[2] obtained by Noyes and Taveau is probably a mixture of optically active isomers of lauronolic acid. The structure of the unsaturated acid melting at 152° - 154°, which was obtained by Noyes and Taveau is unknown. The structure of the unsaturated acid obtained by Noyes and Littleton[3] also was not established.

THE HYDROXY ACIDS.

Of the nine hydroxy acids of this series that have been prepared the structures of seven are known.

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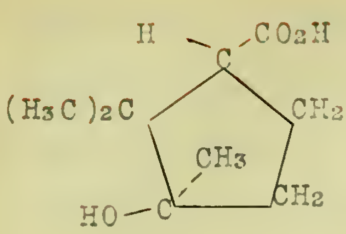
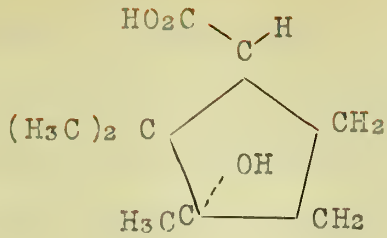
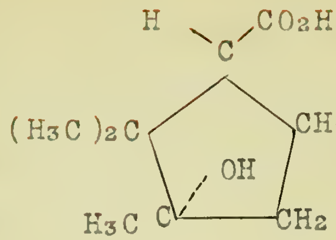
1. Am. Ch. J., 27, 432.
2. Am. Ch. J., 32, 288.
3. J. Am. Ch. Soc., 35, 81.



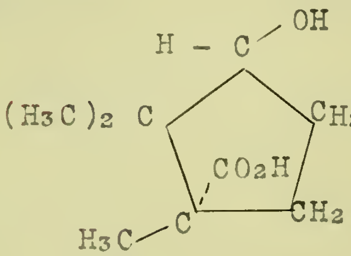
Trans d-Dihydrohydroxy-campholytic Acid[1]
M. P. = 132° - 133°
α_D = +72.05°



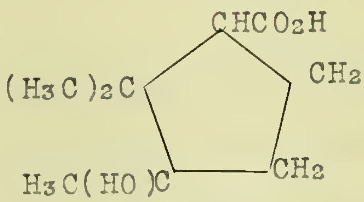
Trans l-Dihydrohydroxy-campholytic Acid[2]
M. P. = 132°
α_D = -70.04°



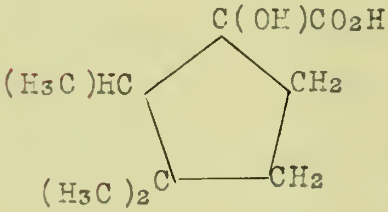
Cis d-Dihydro-hydroxycampholytic Acid
M. P. = 121°
α_D = +50.8°



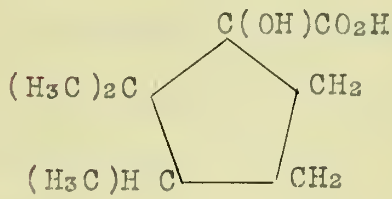
Cis Camphonolic Acid[4]
M. P. = 202° - 203°
α_D = +29.2°



r-Dihydrohydroxycampholytic Acid
M. P. = 173°



α-Hydroxy Dihydroisocampholy-tic Acid
M. P. = 112°



α-Hydroxy Dihydrocampholy-tic Acid

Noyes and Potter (1912) have demonstrated the structure[1] of trans-didihydrohydroxycampholytic acid. It does not readily form a lactone and upon oxidation does not form a ketonic acid. When heated with water at 100° it give chiefly isolaurolene and campholytic acid with only a small amount of campholytolactone. The iso-

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1. This Thesis, Page 10; J. Am. Ch. Soc., 34, 1069; Ber., 33, 2937.
2. This Thesis, Page 15; J. Am. Ch. Soc., 32, 1673.
3. J. Am. Ch. Soc., 34, 1069; Ber., 33, 2939.
4. J. Am. Ch. Soc., 34, 66; Ann., 366, 2.

meric cis-d-dihydrohydroxycampholytic acid[1] readily gives campholytolactone by heating with water at 100° and does not give a ketonic acid by oxidation. Both acids are converted to β-campholytic acid by treatment with dilute sulphuric acid.

The structure[2] of trans-l-dihydrohydrocycampholytic acid follows chiefly from its synthesis. The rotation is practically equal and opposite to that of trans-didihydrohydroxycampholytic acid. When the two are mixed the melting point approaches that of the racemic acid.

The structure[3] of cis-camphonolic acid follows from the fact that it is formed by the reduction of camphonoric acid. It gives cis-camphonololactone by heating at 255°, and is oxidized to camphononic acid by Beckmann's chromic acid mixture.

r-Dihydrohydroxycampholytic acid has been prepared by Noyes and Patterson[4] (1902) by treating the hydrobromide of β-campholytic acid with sodium hydroxide. They also obtained it by decomposing i-dihydroaminocampholytic acid with nitrous acid.

A hydroxy acid derived from isocampholactone has been prepared by Noyes and Taveau[5]. Hydroxylauronic acid[6] has been obtained from the decomposition of aminocamphonanic acid with nitrous acid. Noyes and Shepherd[7] (1899) obtained α-hydroxy dihydroisocampholytic acid by treating the ethyl ester of α-brom-dihydro-β-campholytic acid with barium hydroxide. Noyes and Patterson[8] prepared

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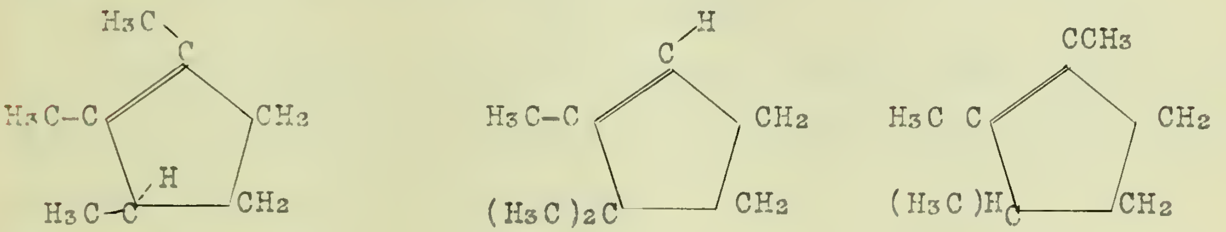
1. J. Am. C. Soc., 34, 1069; Ber., 33, 2939.
2. This Thesis, Page 15; J. Am. Ch. Soc., <u>32</u>, 1673.
3. J. Am. Ch. Soc., <u>34</u>, 66; Ann., <u>366</u>, 2.
4. Am. Ch. J., <u>26</u>, 286; <u>27</u>, 432.
5. Am. Ch. J., <u>32</u>, 290.
6. This Thesis, Page 10.
7. Ber., <u>32</u>, 2291.
8. Am. Ch. J., <u>27</u>, 427.

α-hydroxy dihydrocampholytic acid by treating α-bromo dihydrocampholytic acid with barium hydroxide. The structures of the last two follow from the method of preparation.

THE HYDROCARBONS.

Three hydrocarbons having the general formula C_8H_{14}, which are derived from the camphoric acids, have been prepared.



Laurolene	Isolaurolene	r-Laurolene
B. P. = 120° - 122°	B. P. = 108°-110°	B. P. = 120°-121°
α_D = -29.2° to +28.15°	α_D = (Inactive)	

Laurolene has been obtained in the decomposition[1] of aminocamphonanic acid, by the distillation of calcium camphanate[2], by the slow distillation of camphanic acid[3], either alone or in a slow current of carbon dioxide, and by the distillation of lauronolic acid[4] with soda-lime or zinc chloride. Its optical rotation[5] varies according to the method of preparation. Its structure[6] is well established by synthesis and by the fact that it gives by oxidation with a cold dilute alkaline solution of potassium permanganate a straight chain diketone ($CH_3 - \overset{O}{\overset{\|}{C}} - CH_2 - CH_2 - \overset{CH_3}{\overset{|}{CH}} - \overset{O}{\overset{\|}{C}} - CH_3$) which is optically active.

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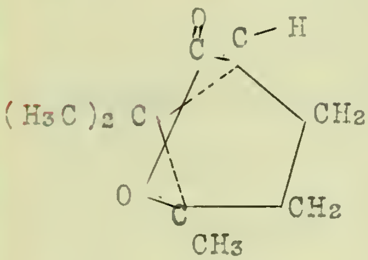
1. This Thesis, Page 9.
2. Ber., 26, 1202; Ann., 163, 336.
3. Ann., 163, 336; 290, 185; 319, 311: 227, 5: J. Ch. Soc., 89, 27
4. J. Am. Ch. Soc., 34, 178.
5. J. Am. Ch. Soc., 31, 670.
6. This Thesis, Page 9 : J. Am. Ch. Soc., 31, 672.

The structure[1] of isolaurolene has been established by synthesis. It has been prepared by distilling copper camphorate[2] from sulfocamphylic[3] acid, and from the decomposition of β-campholytic acid[4], dihydroaminocampholytic acid[5], and dihydrohydroxycampholytic[6] acid.

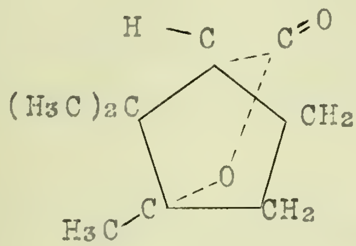
r-Laurolene boils at $120^\circ - 121^\circ$ (752 mm.)

THE LACTONES.

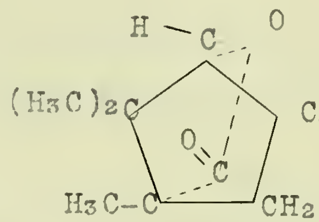
Eight lactones having the general formula $C_8H_{14} - \underset{O}{C} = O$ have been prepared. Of this number the structuras of three are fairly well known.



l-Campholytolactone
M. P.= 228°-230°
M. P.= 114°-115°
α_D = -8.2°



d-Campholytolactone
M.P. = 118°-119°
α_D = $+8.5^\circ$



Cis Camphonololactone
M.P. = 165°-167°
α_D = -22.3°

The structure[6] of d-campholytolactone is based upon its conversion into d-cis-dihydrohydroxycampholytic acid by dilute alkali.

Noyes and Potter (1912) have demonstrated the structure of cis camphonololactone[7] by the following series of reactions:

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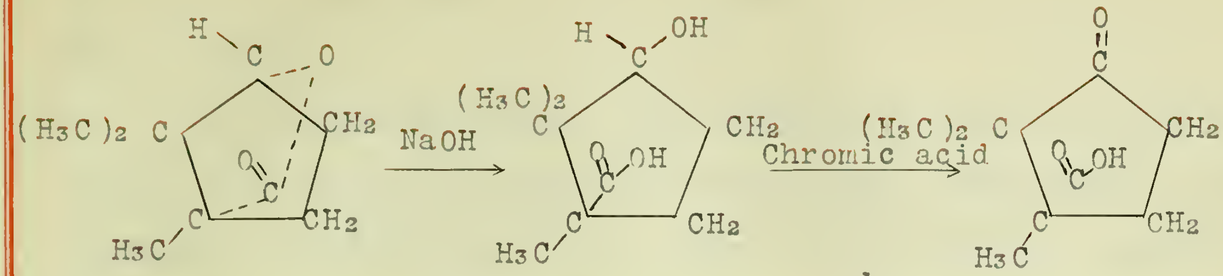
1. This Thesis, Page 11.
2. Jsb.Chem.,(1866), 410.
3. Ber., <u>20</u>, 2957; <u>27</u>, 3470.
4. Bull. soc. chim., (3), <u>19</u>, 703: Ann., <u>319</u>, 307: J. Ch. Soc., <u>89</u>, 29
5. This Thesis, Page 10.
6. J. Am. Ch. Soc., 34, 1074.
7. This Thesis, Page 10; J. Am. Ch. Soc., <u>34</u>, 66.



The structure of l-campholytolactone[1] has been established by converting it into l-campholytolytic acid.

ψ-campholactone was prepared by Lees and Perkin[2] by treating camphoric anhydride with aluminium chloride. It is a mixture for by treatment with barium hydroxide two hydroxy acids are formed, one melting at 113° and the other by 160°.

A lactone[3] has been obtained by the decomposition of isodihydroaminocampholytic acid with nitrous acid. No physical constants were taken.

A lactone[4] has been obtained from dihydrohydroxycampholytic acid, which melted at 115° - 117° and had a specific rotation of $\alpha_D = +121.9^{\circ}$.

The structure of isocampholactone[5] is not known.

The structure of campholactone has not been determined. It is prepared by distilling camphanic acid[6] and by warming lauronolic acid[7] at 100° for a short time with dilute sulphuric acid. M. P.= 49° - 50°. $\alpha_D = -21.6^{\circ}$. With barium hydroxide a hydroxy acid[8]

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1. This Thesis, Page 15.
2. J. Ch. Soc., 79, 332.
3. This Thesis, Page 15.
4. Inaugural Dessertation from the laboratory of Professor Bredt.
5. This Thesis, Page 9.
6. Ann., 227, 10: Ber., 28, 2165: 27, 2114.
7. J. Am. Ch. Soc., 34, 181.
8. Ann., 227, 11: Ber., 33, 2946.

is obtained which melts at $144^\circ - 145^\circ$ and has a rotation of $\alpha_D = +16.0^\circ$.

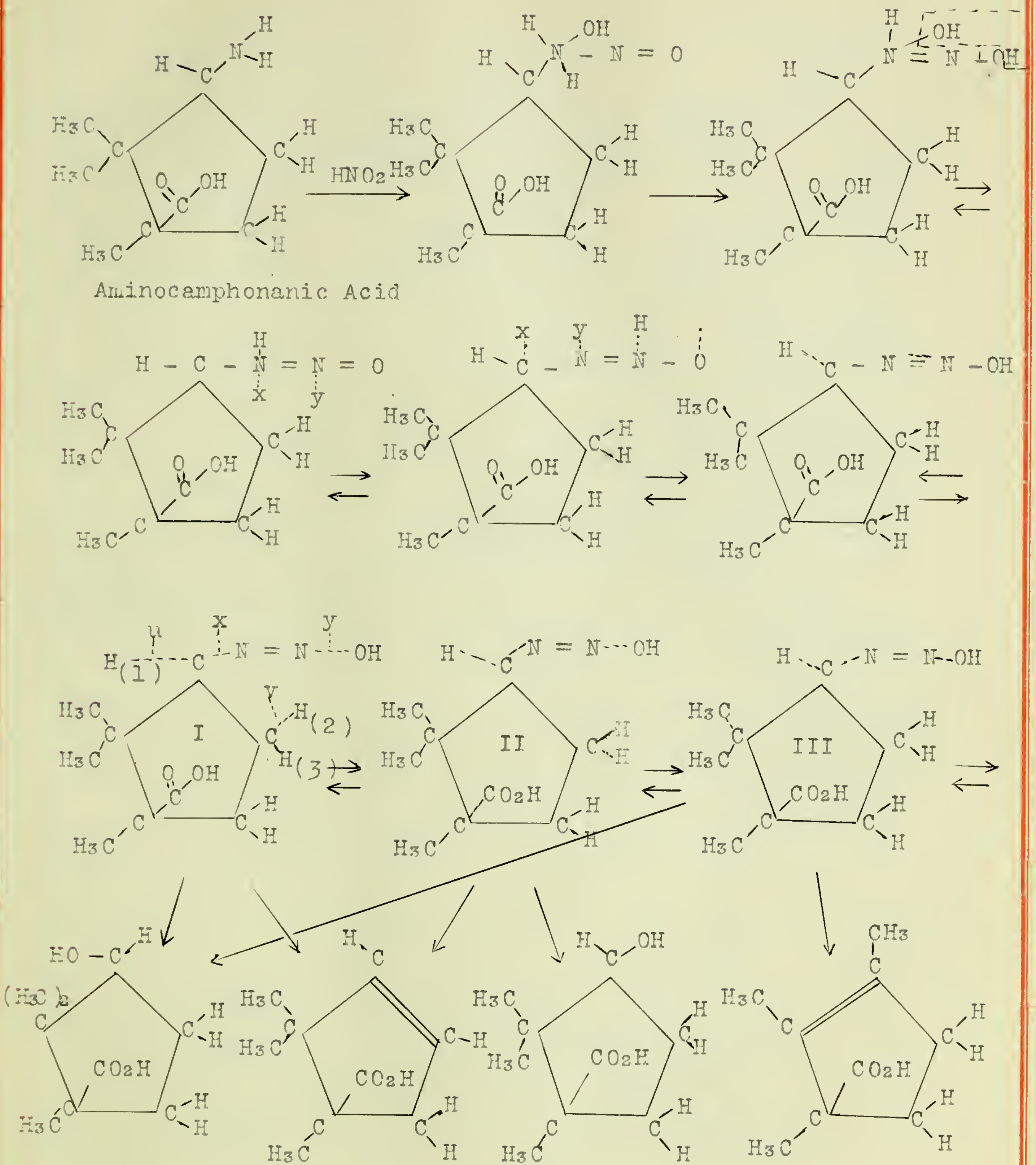
i-α-campholactone has been prepared by Perkin and Thorpe[1] (1904) from magnesium alkyl halide and ethyl ketodimethyl pentamethylene carboxylate. B. P. = $155^\circ - 157^\circ$ (50 mm.). It forms a hydroxy acid which is converted into β-campholytic acid by dilute mineral acids.

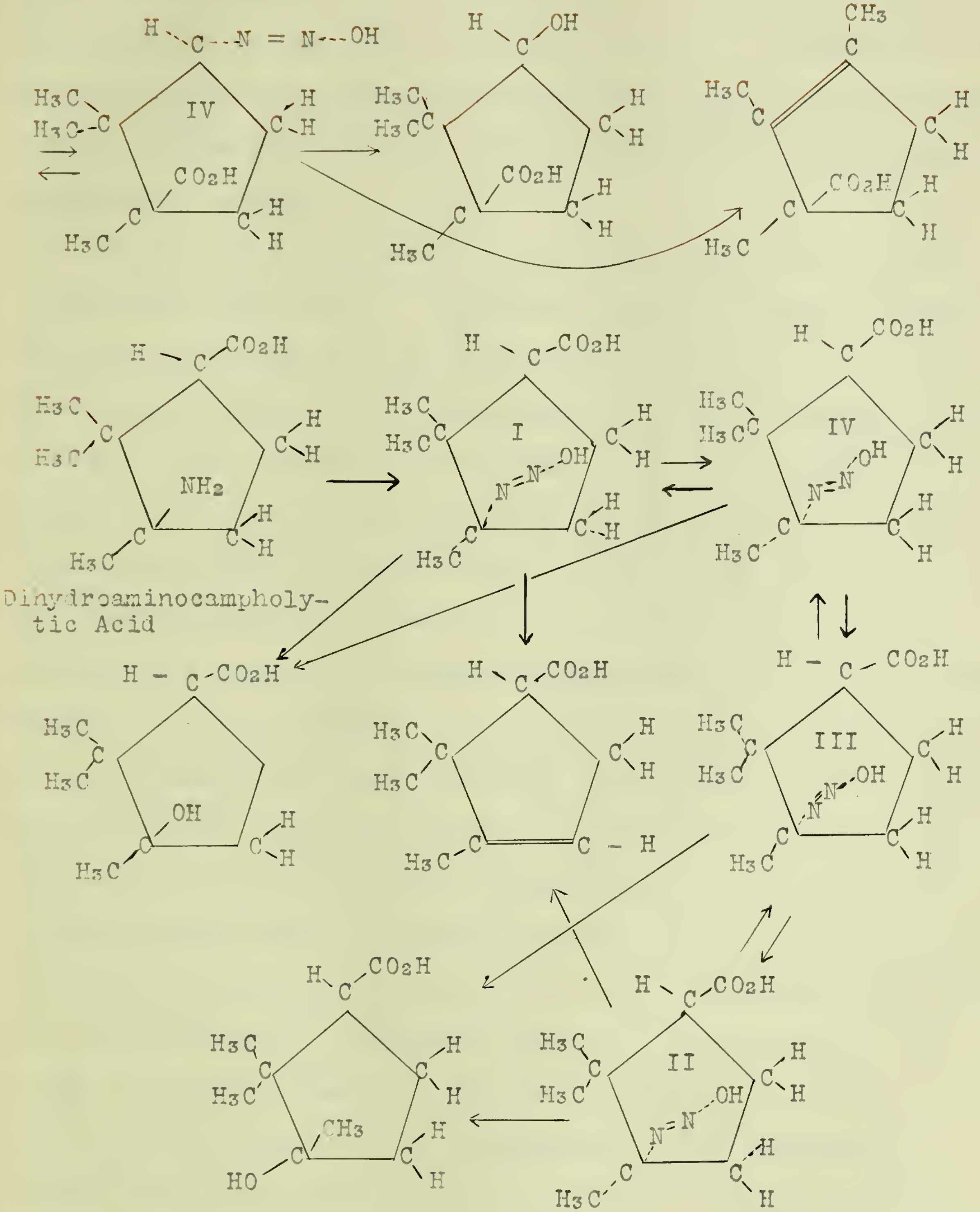
II THEORETICAL.

As indicated in the preceding pages the four amiho acids derived from d-camphoric and l-isocamphoric acids have been decomposed with nitrous acid. In each case a variety of products have been obtained, which affords a problem of no small moment with respect to the determination of their structure and its consequent bearing upon the exact nature of the camphor nucleus.

In the decomposition of the two stereoisomeric acids derived from d-camphoric acid one fact that stands out prominently is that the decomposition is the usual one for aliphatic amines. The second noticeable feature is that in each case intramolecular rearrangements have occurred. It is also interesting to note that a larger number of products is obtained in the case of the α-amino acid. The following is given as the most probable mechanism of the reactions.

1. J. Ch. Soc., 85, 132.


Aminocamphonanic Acid
HNO2
I
II
III


Dihydroaminocampholytic Acid

Each of the unsaturated acids may yield the corresponding hydrocarbon by the loss of carbon dioxide. Thus the above theory would predict a total of two hydroxy acids, two unsaturated acids, and two hydrocarbons from aminocamphonanic acid, and two hydroxy acids, one unsaturated acid, and one hydrocarbon from dihydroamino-campholytic acid.

In the above mechanism the valences x and y are assumed to be coordinated with u and v. When two valences disappear between the two nitrogen atoms to form molecular nitrogen (N = N) two valences must appear between the carbon atom (C_1) and the hydroxyl group on the basis that carbon is tetravalent. This may take place in two ways. On the basis of the kinetic theory and the Van't Hoff hypothesis the atoms are never fixed in their space relations, but are in constant vibration except in the limiting case of absolute zero. Suppose for instance the break to form molecular nitrogen occurs, when the hydrogen atom H_1 in I, which is coordinated with H_2, is at a position whose angle referred to the mean plane of the ring and side chain is θ_1, such that H_1 and OH have the same polarity. Now if OH approaches H_1 in a counterclockwise direction in a mean plane perpendicular to the mean plane of the ring and side chain, OH being the heavier will not stop in its circuitous path until it has broken into the original sphere of influence of H_1, i.e., the space in which H_1 has been vibrating, and will continue to move until it has taken a position opposite to that originally occupied, since H_1 and OH possess opposite polarity and must be in space equilibrium. This is further accentuated by the fact that OH is repelled by H_2. Thus the original amino acid has by the above rearrangement been transformed into the corresponding trans hydroxy acid. If,

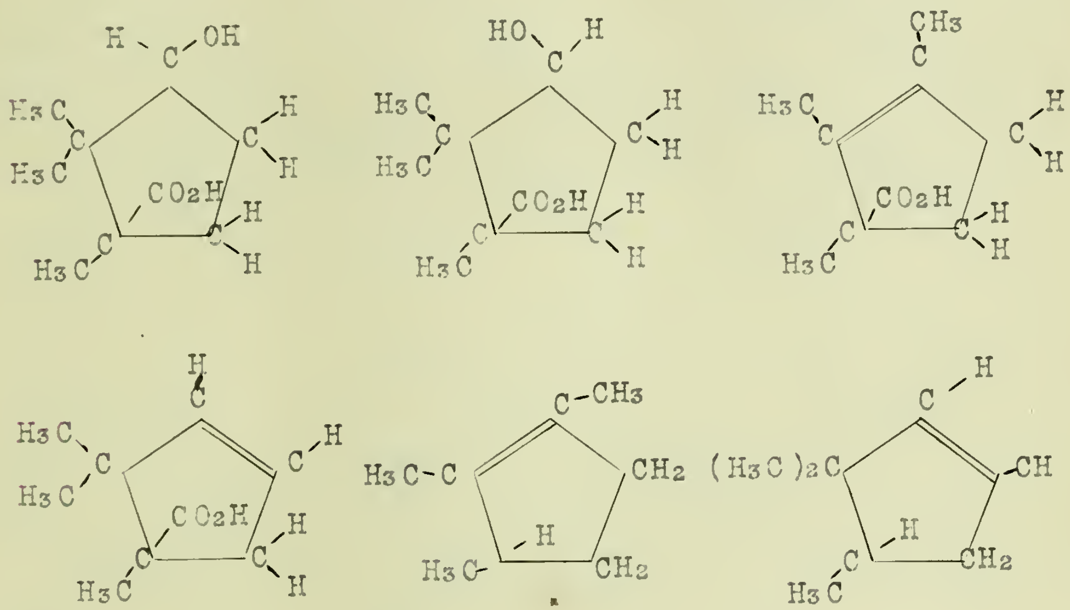
however, (II), H_1 is coordinated with H_3, H_1 and OH will have opposite polarity and consequently will be attracted toward each other. But since H_1 is coordinated with H_3 its motion will be retarded by the latter and likewise OH will be retarded by H_2 so that H_1 and OH will retain their original positions with respect to the plane of the ring and a cis hydroxy acid will result.

Now consider the break to occur when H_1 is at an angle θ_2 to the mean plane of the ring and side chain such that OH moves in a clockwise direction in a mean plane perpendicular to this plane. In the case of (I) this means that OH is being repelled by H_2, since it also possesses the same polarity as H_1, and thus approaches a condition of equilibrium. Under these conditions the polarity of H_1 and H_3 may reverse, in which case H_1 and OH combine to form water andH$_2$ shifts to C_1 so that the two valences disappear between C_1 and C_2. In the cause of (II) where H_1 and OH possess opposite polarity OH is therefore repelled by H_3 and attracted by H_1 and H_2. In the same manner the polarity of H_1 and H_2 is reversed due to the OH group, H_1 and OH combine to form water and H_3 shifts to C_1.

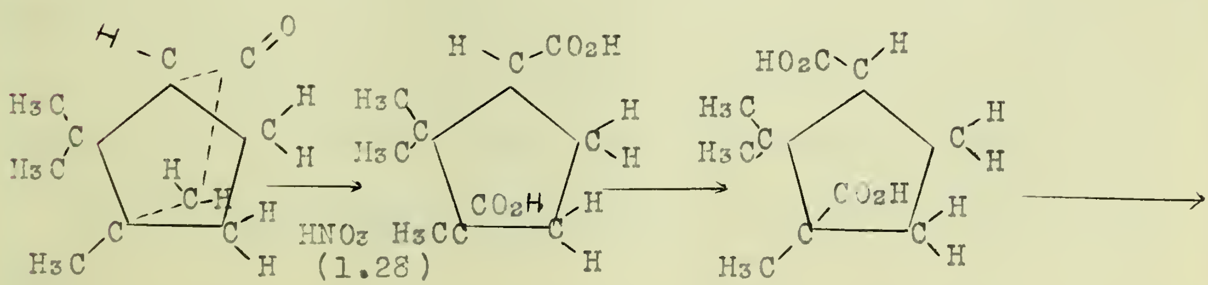
The remaining equilibria may be explained in the same manner. In the case of dihydroaminocampholytic acid the number of products is reduced on account of the methyl radical on the carbon bearing the amino group and the gem dimethyl on one of the adjacent carbon atoms. The formation of hydrocarbons from the unsaturated acids by the loss of carbon dioxide is difficult to explain. At first it might be thought, that since the decomposition of the amino acid is carried out in an acid solution, the reaction might be similar to the acid decomposition of a keto acid, due to the effect of the Δ^3 double union, but better yields of the hydrocarbons are obtain-

ed by decomposing the nitroso derivatives of the anhydrides with alkali. It may be that the loss of carbon dioxide in these reactions is closely related to the loss of carbon dioxide by an ion of an organic acid when it loses its negative charge.

According to the above considerations isoaminocamphonanic acid should give the following products:



The method of Noyes and Littleton[1] was used in the preparation of the materials and is indicated as follows:



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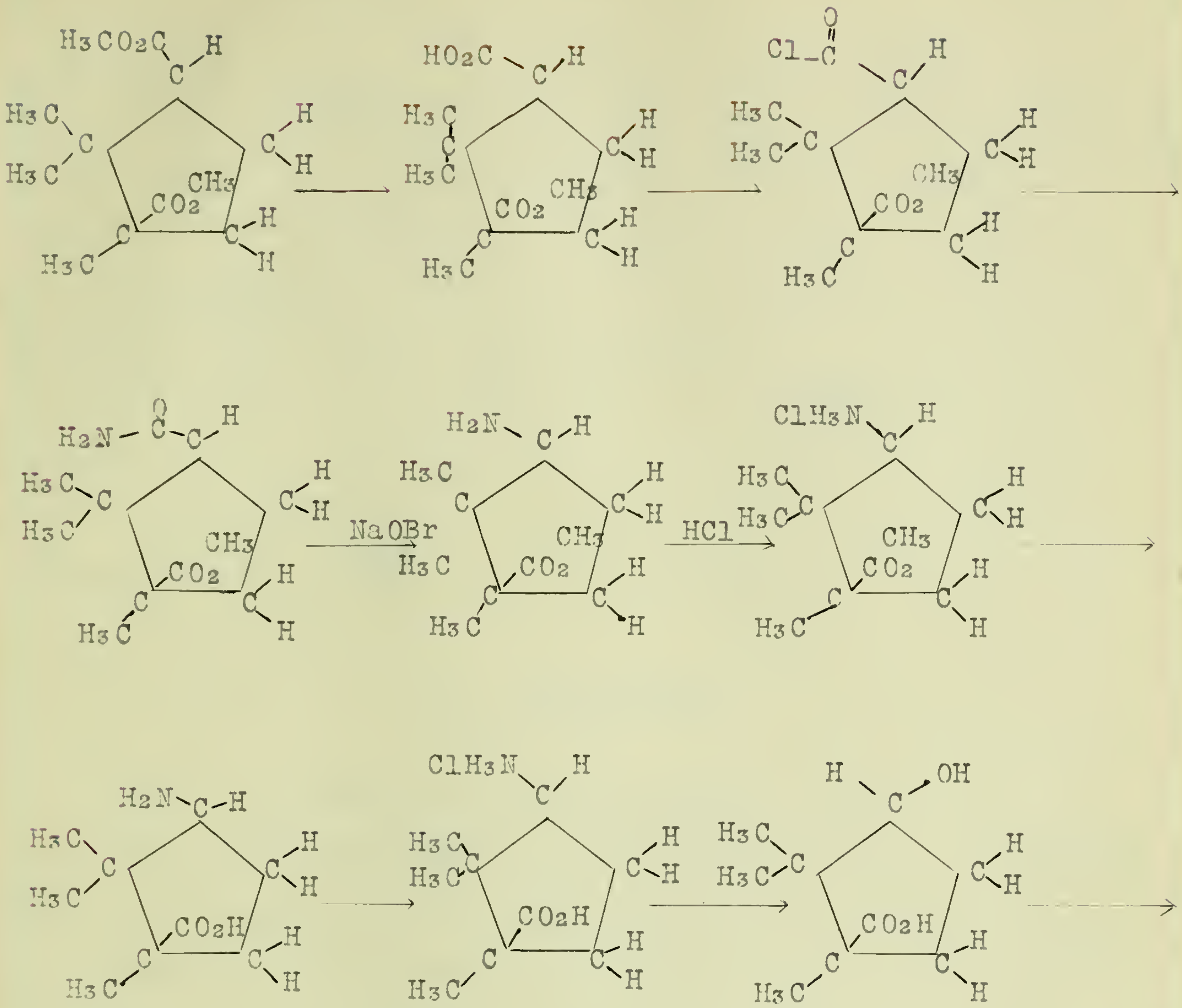
1. J. Am. Ch. Soc., 35, 77.



In this investigation the methyl ester of isoaminocamphonanic acid was decomposed, since the products might then be subject to fractional distillation under diminished pressure without danger of decomposition or rearrangement as in the case of the higher boiling acids. Incidentally this method of procedure should preclude the formation of the hydrocarbons since the degree of dissociation of the ester is practically negligible as compared to that of the free acid.

The mechanism[1] of the formation of the amine ester from the

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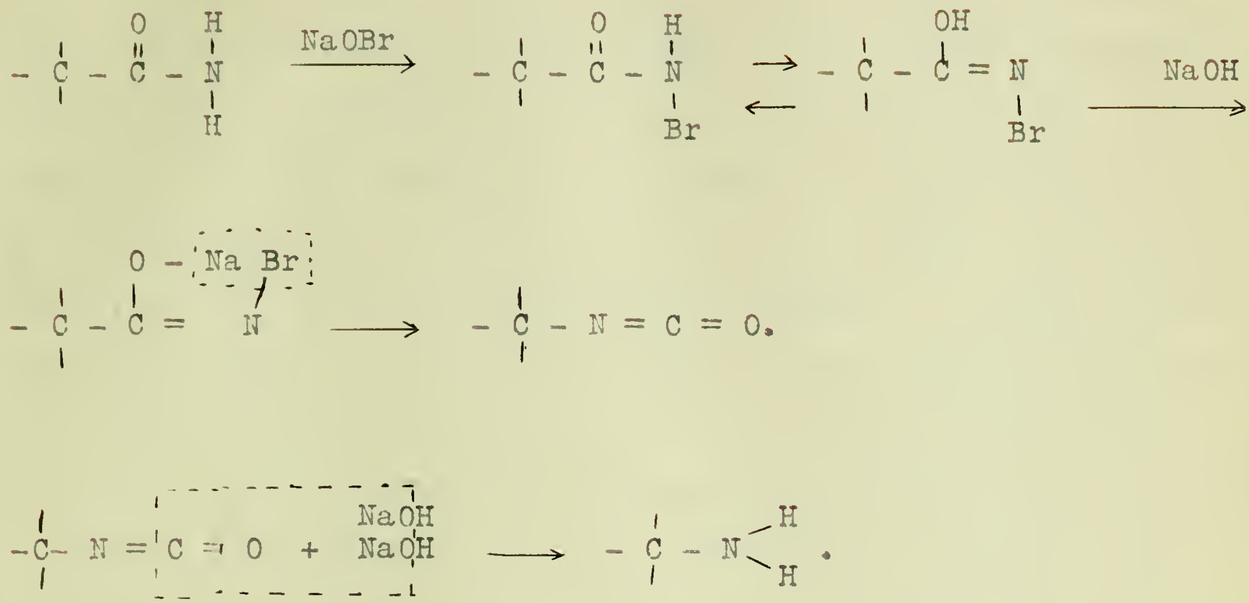
1. Rec., 15, 107: Ber., 35, 2747: 35, 3579.

amide ester is probably as follows:



III EXPERIMENTAL

Preparation of l-Isocamphoric Acid.

Eight sealed tubes each containing 50 grams d-   -camphoric acid, 25 cc. glacial acetic acid and 2 cc. hydrochloric acid (1.20) were heated in a bomb furnace at a temperature of 175° - 185° for ten hours. After cooling the tubes opened under pressure. The semicrystalline concents were poured into a liter of cold water, the tubes being washed out with hot water. The material was stirred as often as needful to prevent solidification into unnecessarily large particles. After allowing to stand for one hour the crystalline material was filtered off with the aid of suction, washed with water, and then dried on the steam bath in a porcelain dish. To this was added the residue from the evaporation of the filtrate. The whole was then finely powdered and thoroughly mixed with one-fourth its weight of acetyl chloride. The mixture was allowed to

stand one hour with occasional stirring. A quantity of water was added and the material filtered off, using suction. After washing free from acetic and hydrochloric acids, the mixture of d-camphoric anhydride and 1-isocamphoric acid was treated with a saturated solution of sodium bicarbonate. The d-camphoric anhydride was filtered off and used in the next charge for the furnace. The 1-isocamphoric acid was precipitated from the solution of sodium 1-isocamphorate by means of hydrochloric acid. After standing ten or fifteen minutes the crystalline material was filtered off, washed and then dried on the steambath. It was dissolved in a small quantity of alcohol, filtering if necessary. The excess of alcohol was boiled out and four or five volumes of boiling water added with vigorous stirring. As the alcohol evaporates spontaneously the acid separates in fine white crystals thruout the liquid. This is a good way to remove the last traces of d-camphoric acid as the solubility of this acid is 6.96 grams per 100 grams of water, while that of 1-isocamphoric acid is only 0.337 grams. M. P. = 170° - 171°. α_D = - . Noyes and Littleton found $\alpha_D = -47.6^{\circ}$. The yield was one-third the weight of the camphoric acid used.

Preparation of α,β-Methyl 1-Isocamphorate.

Noyes and Littleton obtained this ester by boiling a solution of 200 grams of 1-isocamphoric acid, 800 cc. of methyl alcohol and 80 cc. of concentrated sulphuric acid under a reflux for forty-eight hours. It was found that by using the materials in this proportion the yield was inappreciable after five hours, but if twice the quantity of sulphuric acid were used the yield was increased to 60 o/o of the theory. The temperature of the boiling mixture due

to this modification increases from 71° to 78°. The methyl alcohol was distilled first at atmospheric and then under diminished pressure. The mixture of esters was precipitated by the addition of cold water. The water layer was separated and the oily layer was repeatedly shaken in a separatory funnel with a strong solution of sodium bicarbonate to remove the α-methyl ester. The alkaline solution was repeatedly extracted with ether. The ether extract of the α,β-methyl ester was dried with anhydrous sodium sulphate and the ether completely removed on the steam bath with the aid of a capillary under diminished pressure. The ester as obtained by distillation under diminished pressure is a clear oily liquid. B. P. = 140° - 145° (20-27 mm.); 137° - 140° (12 - 14 mm.); 130° - 132° T8 - 10 mm.); 141° - 142° (16 mm.). α_D = -60°. For the pure ester, Noyes and Knight found, B. P. = 146° (27 mm.). α_D = -65.2°.

α-Methyl l-Isocamphorate

The α-methyl ester was precipitated from the above bicarbonate solution with hydrochloric acid and recrystallized from petroleum ether in which it is difficultly soluble. It melted at 88° - 89°. Noyes and Knight found, M. P. = 88°. α_D = -57.9°.

Preparation of β-Methyl l-Isocamphorate.

To 100 grams of α,β-methyl l-isocamphorate was added 100 cc. methyl alcohol and 110 cc. sodium hydroxide (4 o/o excess of one molecule). The mixture was heated on the steam bath under a reflux for 40 minutes. The methyl alcohol was distilled first at atmospheric and then under diminished pressure. The residue was immediately dissolved in water, and the alkaline solution was repeatedly extracted with ether to remove the neutral ester. The

β-methyl ester was precipitated with hydrochloric acid and extracted with ether. After the removal of the ether it remained as a very viscous liquid, which changed to a translucent solid, having the appearance of glue when surrounded by ice water, but it did not crystallize. No attempt was made to distil it under diminished pressure, the probability being that it would undergo decomposition and rearrangement. The yield was 90 o/o - 95 o/o of the theory.

Preparation of β-Methyl α-1-Isocamphoramidate.

The viscous β-methyl ester was warmed gently on the steam bath and then quickly dissolved in a small quantity of ligroin. This solution containing 165 grams of the ester was slowly added from a separatory funnel to a flask fitted with a reflux condenser, and containing 165 grams of phosphorus pentachloride covered with 300 cc. of petroleum ether (B. P. = 25° - 40°). The contents of the flask were protected by means of calcium chloride. When the phosphorus pentachloride had disappeared the solution was diluted with 300 cc. of petroleum ether. This solution was added from a separatory funnel slowly with vigorous stirring to 750 cc. of ammonium hydroxide (0.90), which was kept at a temperature of -10° by a freezing mixture of hydrochloric acid, ice, and water. It is important that the temperature be kept low and that the ligroin solution be dilute, otherwise the yield is very poor. Most of the amide precipitated out in this process and was filtered off. After sucking dry on a plate, it was dissolved in the smallest possible quantity of warm alcohol in which it is very soluble. After filtering four or five volumes of cold water were slowly added with stir-

ring. In this manner 100 grams of a white crystalline product was obtained, which melted at $127^{\circ} - 128^{\circ}$ (cor.). The specific rotation was $\alpha_D = -$. Noyes and Littleton found, $\alpha_D = -54.1$. M. P. $= 126^{\circ} - 127^{\circ}$. It is difficultly soluble in ether. By concentrating the alcoholic liquors the yield was increased to 133 grams.

The ammoniacal liquors were evaporated on the steam bath until ammonium salts began to crystallize, the solution was acidified, and the heavy oil extracted with ether. Upon treatment with sodium hydroxide a white crystalline substance (6 grams) separated, which was identified as the amide by its melting point. Upon acidification of the alkaline filtrate white crystals separated which were insoluble in ether. They were filtered off and washed first with water and then with ether. The melting point was indefinite at about 215°. The ether soluble material, which was obtained as a very viscous liquid probably consisted mainly of the original acid ester.

Preparation of Methyl Isoaminocamphonanate.

To 10 grams of β-methyl α-camphoramidate was added a solution (1.25 mol.) of sodium hypobromite freshly prepared by aspirating the vapor of 10 grams of bromine thru 100 cc. of a 10 o/o solution of sodium hydroxide which was surrounded by ice water. Noyes and Littleton heated the mixture for fifty minutes, but this was found to be unnecessary, and undesirable since the saponification of the ester may become appreciable due to such long continued heating. The contents of the flask should be heated very slowly for the first two or three minutes, frequently giving the flask a gentle rotatory motion. If the operation is carried out properly a

clear yellow solution will result. On further heating the solution became turbid, the yellow color instantaneously disappeared, and an almost colorless oil separated at the surface. The entire time necessary for the completion of the reaction was about five minutes. The contents of the reaction flask were cooled immediately, the alkaline solution extracted three times with small quantities of ether, and the ether extract shaken repeatedly with a dilute (1 : 1) solution of hydrochloric acid. Any unchanged amide remained in the ether layer, and was used again. The amine ester was precipitated from the acid solution by the addition of a slight excess of sodium hydroxide solution. The alkaline solution was extracted repeatedly with ether and after drying with anhydrous sodium sulphate the ether was removed and the amine ester distilled under diminished pressure. The portion boiling at 135° - 138° (20 - 22 mm.) was obtained as a clear mobile oil, which had a fishy odor. The specific rotation was, $\alpha_D = -$. The high boiling residue which partly crystallized in the bulb has not yet been investigated. It is probably a condensation product formed at the temperature of the distillation.

Preparation of the Hydrochloride of Methyl Isoaminocamphonanate.

Dry gaseous hydrogen chloride was conducted to the surface of an ethereal solution of the amine ester, which had not been distilled. The hydrochloride crystallized in long white needles, which melted at 179° - 180° (cor.). $\alpha_D =$. Noyes and Littleton found for the monohydrate, M. P. = 177°. $\alpha_D = -42.03^{\circ}$. The yield was 65 o/o - 70 o/o of the theory calculated on the basis of the amide.

Decomposition of Methyl Isoaminocamphonanate with Nitrous Acid.

The investigation of this decomposition is not yet complete and is being repeated a third time. The results here presented are taken from the first two decompositions.

Twenty-five grams of the above hydrochloride were dissolved in 100 cc. of water. To this was added a solution of 8.4 grams (1.1 mol.) sodium nitrite in 25 cc. of water and a drop of hydrochloric acid to start the reaction, which proceeds with the evolution of heat. After standing over night the yellow oil was extracted with ether and subjected to fractional distillation under diminished pressure. The unchanged amine ester was extracted from the water layer after making it alkaline with sodium carbonate.

The Methyl Esters of the Unsaturated Acids.

The fraction boiling at $86^{\circ} - 88^{\circ}$ (21 mm.) was analyzed with the following results:

	Carbon	Hydrogen
1. Found	70.78 o/o	9.47 o/o
2. Found	71.35 o/o	9.32 o/o
Calculated for $C_8H_{13}CO_2CH_3$	71.37 o/o	9.59 o/o

The rotation for the pure liquid ester was $_{D}^{29^{\circ}} = + 89.65^{\circ}$: for a solution of 1.0005 grams in 11.5 cc. of absolute alcohol $\alpha_D^{29^{\circ}} = +84.93^{\circ}$. $d^{20/20} = .9672$. It is worth while to mention at this point that the products of the first decomposition were first distilled at atmospheric pressure before fractioning under diminished pressure, which may not make the data comparable with that from the subsequent decompositions.

The lower boiling fraction from the second decomposition was

[illegible]

collected at 79° - 84° (16 mm.). The rotation for the pure liquid was $\alpha_D^{27^{\circ}} = +87.64^{\circ}$: for a solution containing 0.08228 grams per cc. of solution $\alpha_D^{28^{\circ}} = +84.71^{\circ}$. $d^{20/20} = 0.9668$.

The substance is without much doubt a mixture of two or more esters having the general formula $C_8H_{13}CO_2CH_3$ as will appear more clearly from a study of the acids themselves.

THE UNSATURATED ACIDS.

The mixture of the methyl esters of the unsaturated acids (5.5 grams) was dissolved in 20 cc. of alcohol and refluxed on the steam bath with 7.2 cc. 30 o/o potassium hydroxide solution (1.1 mol.). After 12 hours the ester was incompletely saponified and was left for 48 hours longer. The flask was broken accidently and part of the material was lost. The alcohol and water were completely distilled off under diminished pressure. The residue was treated with a small quantity of water and solution filtered from any insoluble material. The acids were extracted from the acidified solution with ether and after distilling off the ether the residue was distilled under diminished pressure. One and three-tenths grams of a somewhat mobile liquid was obtained at about 142° (21 mm.) The specific rotation of a solution containing 0.08874 grams per cc. of solution was $\alpha_D^{28^{\circ}} = +84.51^{\circ}$. $d^{20/20} = 1.019$; $d^{25/20} = 1.016$.

	Carbon	Hydrogen
Found	70.46 o/o	8.94 o/o
Calculated for $C_8H_{13}CO_2H$	70.07 o/o	9.15 o/o

The lower boiling fractions from the second decomposition were saponified and the acid obtained in the same manner. The product

TABLE I

Fraction	Boiling Point	Pressure	Temperature of Bath
A - I	- 90°	22 mm.	120° - 125°
II	90 - 100	25 mm.	150
III	100 - 120	23 mm.	- - -
IV	120 - 135	22 mm.	175 - 200
V	135 - 170		
B - I	- 95		
II	90 - 100	22 mm.	125
III	100 - 129		
IV	129 - 145		
V	145 - 170		
C - I	90 - 100	22 mm.	120
II	100 - 125	20 mm.	150
III	125 - 135	20 mm.	160
D -II	100 - 120	20 mm.	140
III	120 - 130	20 mm.	160
E - I	- 90	20 mm.	100 - 120
II	90 - 100	20 mm.	125
F - I	83 - 90	20 mm.	100 - 110
II	90 -	20 mm.	120
G - I	84 - 88	20 mm.	105 - 110
H - I	- 86	20 mm.	105
II	86 - 88	20 mm.	105 - 110

TABLE II

Fraction	Boiling Point	Pressure	Temperature of Bath
A - I	- 124	25 - 23 mm.	120° - 160°
II	124 - 155	22 mm.	150 - 190
B - I	- 105	20 mm.	105 -- 130
II	105 - 140	20 mm.	140 - 170
III	140 - 170	20 mm.	170 - 300
C - I	82 - 93	21 - 20 mm.	110 - 125
II	93 - 125	20 mm.	140 - 165
III	125 - 141	20 mm.	175 - 185
D - I	82 - 88.5	20 mm.	105 - 125
III	100 - 110	19 mm.	130 - 140
III	110 - 120	18 mm.	145 - 160
IV	125 - 135	18 mm.	160 - 170
E - I	80 - 88	18.5 mm.	105 - 120
II	90 - 100	18.5 mm.	
III	100 - 110	19 mm.	130 - 140
IV	110 - 120	19 mm.	150 - 165
V	123 - 134	18 mm.	155 - 165
F -II	90 - 105	16 mm.	130 - 135
III	105 - 110(1.5 grams)	16 mm.	140
IV	110 - 127	17 mm.	160
V	127 - 134	17 mm.	160 - 180
G -IV	115 - 125(2.3 grams)	17.5 mm.	145 - 160
V	125 - 135(3.9 grams)	17 mm.	155 - 165
H - I	79 - 84(11.6 grams)	16 mm.	105 -- 115
II	85 - 100(.8 grams)	16 mm.	115 - 130

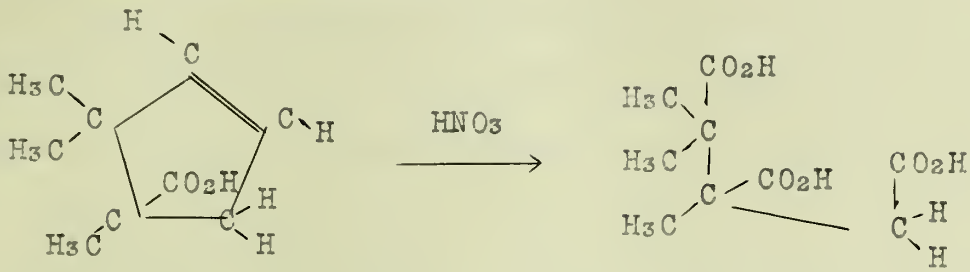
seemed to be more mobile than that from the first decomposition. The boiling point was $145^\circ - 147^\circ$ (25 mm.), and the yield was 5.2 grams.

	Carbon	Hydrogen
Found	69.68 o/o	9.33 o/o
Found	69.83 o/o	9.15 o/o
Calculated for $C_8H_{13}CO_2H$	70.07 o/o	9.15 o/o

The liquid substance gave a specific rotation of $\alpha_D^{31^\circ} = + 113.21^\circ$. A solution in absolute alcohol containing 0.08352 grams per cc. of solution gave, $\alpha_D^{30^\circ} = +88.36$. $d^{20/20} = 1.014$.

Before it was definitely shown that the above substance was a mixture of at least two isomeric acids an attempt was made to establish its structure by oxidation. Five-tenths of a gram of the acid, 2 cc. of water and 3 cc. of nitric acid (1.40) were placed in a long narrow test-tube and the mixture heated on the steam bath for a half hour. The reaction was vigorous at first and solution resulted in a few minutes. The contents of the tube were poured into a porcelain dish and evaporated to dryness. A light yellow crystalline residue was obtained, which dissolved to a dark orange colored solution with 10 o/o sodium hydroxide, indicating the presence of nitro compounds. After filtering a dilute solution of barium chloride was added and the solution filtered. The filtrate was heated to boiling and the precipitate, presumably barium l-camphoronate, was filtered off. After drying thoroughly a few drops of hydrochloric acid were added and then allowed to evaporate on a watch glass. The dry residue was treated with a little absolute alcohol to dissolve the camphoronic acid. The alcohol was evapo-

rated and the residue dissolved in a few drops of water and allowed to crystallize on a watch glass. The crystals melted indefinitely at about 150°. l-Camphoronic acid treated in the same manner melted indefinitely at about the same temperature. As the yield was small this method of procedure was discontinued. The reaction should take place as follows:



Five-tenths of a gram of the acid and about twice this quantity of anhydrous zinc chloride were placed in a very small distilling bulb and slowly distilled. The distillate was distilled with steam by which process the volatile hydrocarbon was separated from any unchanged acid. The light oil was drawn off by means of a capillary in a narrow test-tube. After drying with anhydrous sodium sulphate the boiling point as determined by the equilibrium method was 120°. Noyes and Burke obtained a boiling point of 120°-121°. It is then clear that the acid consists almost entirely of lauronolic acid, or in addition to lauronolic an acid which in the decomposition with zinc chloride rearranges to lauronolic acid.

As a further means of identification the preparation of the calcium salt was tried. The acid was dissolved in a very dilute solution of alcohol in water and warmed on the steam bath with an excess of very finely powdered calcium carbonate until upon shaking the evolution of carbon dioxide was reduced to a minimum. The filtrate was concentrated, any insoluble material was filtered off,

and the resulting filtrate was slowly evaporated on the steam bath during which process the calcium salt crystallized. The salt, which was found to be neither efflorescent or deliquescent, was dried between filter papers and analyzed immediately for calcium and water of crystallization. After many unsuccessful attempts to obtain check results, in which the water of crystallization varied from two to four molecules, the evaporation from two to four molecules, the evaporation in an open porcelain dish was discontinued and carried out in a small Erlenmeyer flask instead. By this method the crystals separated in the interior of the liquid instead of separating at the surface. Two distinct kinds of crystals were obtained, one in the form of thin translucent plates, and the other in the form of large rosettes of radiating fibers. The results of the analysis follow:

	Time	Temperature	Water	Calcium
Plates	(abt. 2 hrs.)	110°-115°	13.43%	9.99%
Calculated for $C_8H_{13}CO_2H.3H_2O$			13.50%	10.01%
Rosettes	150 min.	105°-110°	9.50%	11.87%
Calculated for $C_8H_{13}CO_2H.2H_2O$			9.42%	11.58%

The calcium is calculated on the basis of the anhydrous salt.

Bredt who prepared the calcium salt of lauronolic acid in this way found two molecules of water of crystallization. Noyes and Knight in preparing the salt by evaporation in an open dish so that the crystals formed at the surface found three molecules.

The weight of the rosettes was nearly four times that of the plates. In the case of the rosettes the anhydrous salt obtained from the determination of the water of crystallization was treated

with dilute hydrochloric acid and extracted with ether repeatedly. After drying, the ether extract was transferred in portions to a 5 cc. volumetric flask and allowed to stand in vacuo for three hours. The specific rotation was $\alpha_D^{29°} = +83.4°$ for a solution in absolute alcohol containing 0.0779 grams in 5 cc. of the solution.

In all probability the substance is a mixture of the two unsaturated acids predicted by the theory, but this has not been proved to be the case. However one of the acids has been identified as lauronolic acid by the formation of the calcium salt and by decomposing it into laurolene.

The Methyl Esters of the Hydroxy Acids.

The fraction from the second decomposition boiling at 125° - 135° (17 mm.) which was obtained as a heavy colorless oil, was analysed.

	Carbon	Hydrogen
Found	65.08 o/o	9.70 o/o
Calculated for $C_8H_{14}(OH)CO_2CH_3$	64.46 o/o	9.80 o/o

The rotation for the liquid ester was $\alpha_D^{28°} = +10.35°$: for a solution in absolute alcohol containing .0828 grams per cc. of solution $\alpha_D^{26°} = +10.26°$. $d^{20/20} = 1.061$.

The Hydroxy Acids.

After fractionally distilling under diminished pressure the higher boiling fraction was shaken with a 30 o/o sodium carbonate solution to remove the acid substances. The aqueous solution was extracted repeatedly with ether, the ether was boiled out by warming on the steam bath, and the acid was precipitated as a crystal-

tracted with ether from which it crystallized in needles. The specific rotation for a solution in absolute alcohol containing .0647 grams per cc. was $\alpha_D^{27^\circ} = -16.84^\circ$. Upon evaporation of the alcohol the crystals melted at 161° - 162° (cor.). Noyes and Littleton[1] found, M. P. = 160° - 162°. $\alpha_D = -16.1^\circ$. Noyes and Potter[2] found, $\alpha_D = -22.3^\circ$. M. P. = 165° - 167°. Bredt[3] found, $\alpha_D = -16.8^\circ$.

The acid was further identified as cis-camphonolic acid by oxidation. Five-tenths of a gram of the acid was placed in a test-tube and to this were added 3 cc. of Beckmann's chromic acid mixture.[4] After standing over night the mixture was diluted with 2 cc. of dilute sulphuric acid (1 : 1) and allowed to stand 48 hours longer. The dark colored solution was then diluted with two or three volumes of water and extracted with ether. The ether residue was dissolved in benzene and evaporated on the steam bath in a test-tube until crystallization began. The crystalline product obtained by diluting with an equal volume of petroleum ether melted at 228° (cor.). The specific rotation was, $\alpha_D^{30^\circ} = -3.9^\circ$ for a solution in absolute alcohol containing .0230 grams per cc. of the solution. Noyes and Potter found for camphononic acid, M. P. = 229° - 230°: $\alpha_D^{28^\circ} = -3.9$. Lapworth and Lenton found, M. P. = 228°. Lapworth and Chapman[5] found, M. P. = 228°. Walker and Henderson[6] found, M. P. = 228° (cor.). The acid is therefore cis-camphonolic acid.

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1. J. Am. Ch. Soc., <u>35</u>, 80.
2. J. Am. Ch. Soc., <u>34</u>, 66.
3. Ann., <u>366</u>, 2.
4. Ann., <u>250</u>, 325.
5. J. Ch. Soc., <u>75</u>, 1000.
6. J. Ch. Soc., <u>69</u>, 755.

line solid by the addition of hydrochloric acid. Upon recrystallization from hot water containing a little alcohol a perfectly white crystalline product was obtained which melted sharply at 87°. The portion soluble in dilute sodium hydroxide solution and insoluble in a sodium carbonate solution was negligible.

The portion of the higher boiling fractions insoluble in a potassium carbonate solution (3 grams) was dissolved in alcohol and saponified for 24 hours on the steam bath, when the flask cracked and the contents were lost.

The fractions boiling from 105° - 135°, which were obtained from the second decomposition, were heated under a reflux with a 30 o/o potassium hydroxide solution (1.1 mol.) for 48 hours on the steam bath. The alcohol was distilled on the steam bath under reduced pressure. The residue was dissolved in water, filtering from any undissolved material and extracting the alkaline filtrate with ether. The solution was acidified with hydrochloric acid and extracted with ether. After drying the hydroxy acid was precipitated by the careful addition of petroleum ether. When the fractional crystallization had been repeated a fourth time, the fraction most insoluble in ligroin gave a constant melting point of 195.5° (cor.). The specific rotation for a solution in absolute alcohol containing .0912 grams per cc. of the solution was, $\alpha_D^{27^\circ} = +32.12^\circ$. Noyes and Potter found, M. P. = 202° - 203°. $\alpha_D = +29.2^\circ$. Bredt found, M. P. = 197° - 198°. $\alpha_D = +29.7^\circ$.

Five-tenths of a gram of the acid was heated in a bath of paraffin at a temperature of 255° for 15 minutes. A white crystalline substance sublimed on the sides of the tube. This was shaken with a potassium carbonate solution to remove any unchanged acid and ex-

The fraction most soluble in petroleum ether from the above factional crystallization was obtained as a very viscous oil which would not crystallize even after seeding with the crystals from the higher boiling fractions. The calcium salt was obtained as an amorphous substance having the consistency of glue. From a solution of this salt the silver salt was precipitated by the addition of a silver nitrate solution. It rapidly turned black and therefore was not analyzed. The copper salt precipitates as a green waxy substance.

The free acid from the higher boiling fractions which crystallized in the receiver was dissolved in a dilute sodium hydroxide solution and the alkaline solution extracted with ether. The ether was boiled out of the water layer, which was then acidified with hydrochloric acid. The crystalline product was extracted with ether and crystallized from a mixture of ether and petroleum ether. By slow crystallization some large monoclinic prisms were obtained, the largest being two centimeters in length. They were completely soluble in a dilute sodium carbonate solution. The specific rotation of a solution in absolute alcohol containing .0455 grams per cc. of the solution was, $\alpha_D^{28^\circ} = +72.08^\circ$. M. P. = 87° (cor.).

An attempt was made to convert it into the lactone by heating at 255°. The product dissolved easily in a dilute potassium carbonate solution, and melted rather indefinitely at about the same temperature. The specific rotation of a solution in absolute containing .04247 grams per cc. of the solution was $\alpha_D^{27^\circ} = +68.5^\circ$, showing that the acid was mostly unchanged.

Thus thinking that the acid was merely a trans isomer of cis-camphonolic acid an attempt was made to oxidize it to camphononic

acid in the manner before described. The product melted rather indefinitely at about 79° - 80°.

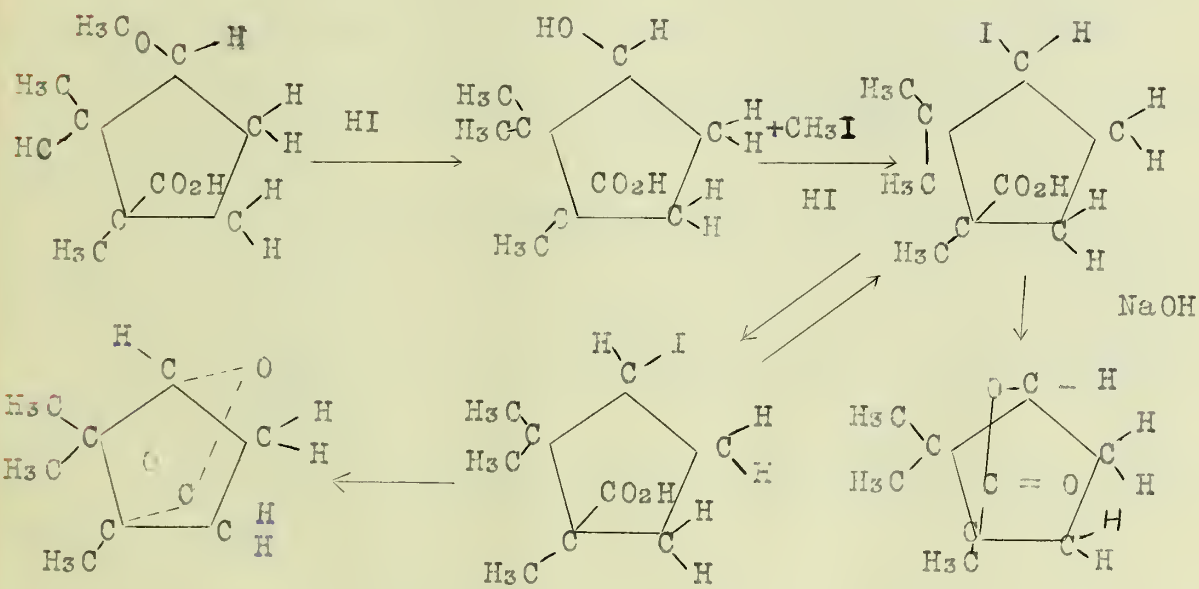
An attempt was made to prepare the hydroiodide with a view to obtaining an unsaturated acid which might give some indication of its formula. Five-tenths of a gram of the acid which had been crystallized from water was dissolved in carbon disulphide in which it is easily soluble. Gaseous hydrogen iodide was passed into the solution until the dark brown precipitate which at first formed no longer increased in amount. The product was extremely unstable and the melting point was indefinite at 60° - 65°, after washing with petroleum ether. When the product had stood over night in a desiccator, during which time it partly decomposed, it was warmed on the steam bath with a 5 o/o solution of sodium carbonate. A black waxy substance separated which gradually lost its color until a white crystalline product remained. It was extracted with ether from which it crystallized in needles, melting at 160° - 161° (cor.), but upon standing the melting point was indefinite at about 150°. The small amount of residue from the carbon disulphide liquors melted indefinitely at 70° - 75°. This was treated with a dilute sodium hydroxide solution, and extracted with ether. The crystals upon evaporation of the ether melted at 79° - 80°.

The structure of this acid is still unsettled. The substance melting at 160° - 161° is probably cis-camphonololactone and that melting at 79° - 80° the lactone of the trans isomeric acid. The former is probably formed by a Walden inversion, while in the latter case no rearrangement has occurred. The acid probably contains no free hydroxyl group since it does not give a keto acid by oxidation and from the (fact ?) that it gives cis-camphonololactone by

the decomposition of the hydroiodide. The analysis also does not correspond to a hydroxy acid but to an ether acid.

	Carbon	Hydrogen
Found	63.82 o/o	9.84 o/o
Calculated for $C_8H_{14}(O-CH_3)CO_2H$	64.50 o/o	9.67 o/o

It is without doubt a chemical individual since the melting point of the acid obtained by both methods of crystallization is the same. The above relations may be represented as follows



The study of these compounds is being continued with a view toward obtaining more positive evidence concerning their structure.

IV CONCLUSIONS.

It may be stated that the chief conclusions to be drawn from the work are as follows:

1. It has been definitely shown that when methyl iso aminocamphonanate is decomposed with nitrous acid the methyl esters of two unsaturated acids of the general formula $C_8H_{13}CO_2H$, and a methyl ester of one hydroxy acid of the general formula $C_8H_{14}^{\diagup OH}CO_2H$ are obtained. A fourth compound, possibly the methyl ether of a hydroxy acid of the general formula $C_9H_{14}^{\diagup OH}CO_2H$ is also obtained.

2. One of the unsaturated acids is lauronolic acid.

3. One of the hydroxy acids is cis-camphonolic acid.

4. The unsaturated and hydroxy acids are formed in approximately equal amounts.

5. The Method of preparation of α, β methyl 1-isocamphorate has been improved.

6. The method of preparation of methyl isoaminocamphonanate has been improved.

7. A method of separation of the unsaturated acids has been discovered.